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(73) Proprietor: **VISKASE CORPORATION**
6855 West 65th Street
Chicago, Illinois 60638 (US)

(72) Inventor: **Juhl, Roger Leeroy**
32 Woods Edge Drive
Asheville,
North Carolina 28803 (US)
Inventor: **Tijunelis, Donatas**
419 Weidner Road
Buffalo Grove,
Illinois 60090 (US)
Inventor: **Lustig, Stanley**
561 Lakewood Boulevard
Park Forest,
Illinois 60466 (US)

(74) Representative: **Weinhold, Peter, Dr. et al**
Patentanwälte
Dr. Weinhold, Dannenberg,
Dr. Gudel, Schubert
Siegfriedstrasse 8
D-80803 München (DE)

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Description

This invention relates to an extruded thermoplastic film containing a modifier which is transferable from the film to a receiving surface in fluid transfer relationship with the film, as for example a plastic bag containing liquid smoke which is transferred to the outer surface of meat during hot water cook-in of the meat within the bag.

Foods are often processed, i.e. cooked, in a thermoplastic film package by for example at least partially immersing the package in hot water or placing the package in a steam-heated environment. The processed food package may then be refrigerated until the processed food is to be consumed, and then reheated. Alternatively the processed food may be immediately removed from the thermoplastic film enclosure, as for example a casing or bag for consumption. US-A 4,784,863 describes such a cook-in system. Also described therein is a three layer film prepared by coextrusion, biaxial orientation to impart heat shrinkability, and then irradiation of the biaxially oriented film to widen the heat sealing temperature range and improve certain physical properties. The film may for example comprise an ethylene-vinyl acetate (hereafter "EVA") inner layer, a vinylidene chloride copolymer oxygen barrier-core layer and an EVA outer layer.

It may be desirable to apply a modifier to the outer surface of the processed food. For example, if the food is poultry or ham, it may be desirable to impart smoke color and flavor to the cooked poultry or ham outer surface. This of course may be accomplished in a separate step by placing the processed food in a smoke house. For distribution this requires removal of a smoke-permeable enclosure from the smoked, processed food body and repackaging in an oxygen barrier type film enclosure for extended shelf life.

It would be desirable to provide a film article which can be used as an enclosure for processing enclosed food and also as a vehicle for simultaneously transferring modifiers such as liquid smoke to the food surface during processing.

Various problems have been encountered in attempts to provide such a film article. For example, powdered smoke concentrate was added to the inside surface of the inner EVA layer of an oxygen barrier type multilayer film of the type described in the aforementioned US-A-4,784,863. Hams processed in bags fabricated from this film had a moderate smoke flavor but the smoke color on the processed ham outer surface was highly non-uniform because the powder tended to accumulate in pockets on the ham surface during stuffing.

Another approach was to blend commercially available smoke-flavored polymer concentrates with the EVA resin used as the inner layer of the above type coextruded multi layer film. Cook-in tests using bags fabricated from film with this inner layer blend did not transfer smoke color or flavor to the processed ham. Similarly there was no smoke color or flavor transfer to low fat meat bologna processed in casings prepared from this film.

Still another attempt to prepare a film with a transferable modifier involved melt blending a glycerine-based liquid smoke concentrate with the EVA resin used as the inner layer of the multilayer film. This caused the primary film discharged from the extruder to delaminate before biaxial orientation. Orientation was not possible.

A further approach was to mix equal weights of liquid smoke concentrate and powdered silica, then melt blending the liquid smoke-loaded powder with the EVA resin used as the film inner layer. Silica is of course a well-known absorbent. A multi layer film of the vinylidene chloride oxygen barrier type was produced having a smoke odor. However, very little smoke color or flavor was transferred to meat during cook-in tests using bags fabricated from this film.

A difficulty with these approaches was that for these tests the modifier was wood-derived smoke, and at extrusion temperatures for these particular multilayer films [about 177°C (350°F)], the odor and taste components of the smoke are volatile and reactive, and do not survive extrusions in sufficient quantity to impart color or flavor to meat.

Accordingly, in other tests well-known absorbents such as starch, gypsum and thermoset crosslinked water soluble resin were blended with the EVA resin, and the multilayer film was coextruded. Then the film was contacted with liquid smoke for absorption thereby. However, the liquid smoke absorbency of these EVA-absorbent blend inner layer-type films was so low that transfer in the presence of water to contiguously associated surfaces for example food bodies, would be negligible.

US-A-4 865 901 discloses a thermal transfer printing ribbon for printing on a print-receiving material, said ribbon comprising a support element and an ink-layer including a thermal melting ink which is a blend comprising a binder and a colorant (particularly carbon black), said binder comprising EVA and a highly viscous resin of a certain melt viscosity (e.g. poly(ethylene oxide)). In the course of printing the entire ink-layer (i.e. colorant and binder) of said ribbon is transferred onto the print-receiving material.

An object of this invention is to provide an extruded film article comprising a blend of (i) a thermoplastic polymer selected from polyolefins, polyurethanes, ionomers, polyamides, polyesters, vinylidene chloride copolymers and hydrolyzed ethylene-vinyl acetate-copolymers, (ii) poly(ethylene oxide) having an average molecular weight of at least 70,000 and (iii) a modifier selected from colorants, fragrances, flavorents, colorant-fragrances, antioxidants for controlling the rancidity of foods, antimycotic agents, biocides, odor absorbents and surface energy modifiers, said modifier being absorbed in said blend and being transferable from said film to a receiving surface in fluid transfer relationship with said film.

Another object of the invention is a biaxially oriented and heat shrinkable multilayer extruded film comprising a vinylidene chloride copolymer core-barrier layer; a blend second layer adhered to one side of the core layer and comprising components (i) to (iii) as defined in claim 1 wherein component (i) is a polyolefin, said modifier (iii) being transferable from said blend second layer of the multilayer film to a contiguous receiving surface in the presence of water; and a polyolefin third layer adhered to the other side of said core layer opposite to said one side.

A further object of the invention is a method for making such a modifier-transferable film article.

Another object is to provide an enclosure such as a casing or bag, fabricated from the extruded film article, which will transfer the modifier to the outer surface of a body encased in the enclosure and in fluid association with the film inner surface.

A still further object is to provide a processable food package comprising a multi layer oxygen barrier type film enclosure containing a modifier, the enclosure being filled with processable food, wherein the modifier is transferable from the film enclosure to the food outer surface during in situ processing.

Still another object is a method for making a modified food package of the type hereinabove described.

Other objects and advantages of the invention will be apparent from the ensuing disclosure and appended claims. As will be explained hereinafter, this invention achieves all of the aforedescribed objects in an unexpected and efficient manner.

Poly (ethylene oxides) with molecular weights of at least 70,000 and up to 5×10^6 are dry, free-flowing white powders, completely soluble in water at temperatures up to about 98 °C. They have crystalline melting points from 63 to 67 °C. The chemical structure of poly (ethylene oxide) resin is

$$(O\text{-}CH_2\text{-}CH_2)x$$

Because of the very high molecular weights of these resins, the concentrations of reactive end groups is extremely small, so there is no end group reactivity.

Poly (ethylene oxides) are used as thickening agents in water and will reduce the turbulent frictional drag of the water in which they are dissolved by up to 80%.

Poly (ethylene oxide) is known as an additive to thermoplastic films to promote biodegradability. It is susceptible to severe auto-oxidative degradation and loss of viscosity in aqueous solutions.

According to the Handbook of Water-Soluble Gums and Resins by Robert C. Davidsons, (published by McGraw-Hill Book Company, 1980) the mechanism involves the formation of hydroperoxides that decompose and cause cleavage of the polymer chain. The rate of degradation is increased by heat, ultraviolet light, strong acids, or certain transition metal ions.

Accordingly, to the best of our knowledge poly (ethylene oxides) have not heretofore been used in thermoplastic films to be extruded, wherein the poly (ethylene oxide) is included to perform an absorption function in the extruded film.

Nevertheless it has unexpectedly been discovered that poly (ethylene oxides) may be blended with certain types of thermoplastic polymers and extruded to form water swellable films. A modifier (hereinafter defined) is either also blended with the poly (ethylene oxide) and thermoplastic polymer prior to film extrusion or absorbed into the as-extruded film. The modifier is transferable from the film to a receiving surface in fluid transfer relationship with the film. More particularly, this invention in its article aspect comprises a blend of a certain thermoplastic polymer (defined hereinafter) and a poly (ethylene oxide) having an average molecular weight of at least 70,000, and a certain modifier (defined hereinafter) absorbed in said blend. The modifier is transferable from the film to a receiving surface. The film and receiving surface are preferably in contiguous association and the transfer is preferably in the presence of water. Suitable receiving surfaces include meat, poultry, carbohydrate and cheese.

Another aspect of the invention is a thermoplastic bag formed of an extruded film comprising the above blend. The modifier is transferable from the film to a product receiving surface within the bag. Alternatively, a thermoplastic casing may be formed from the same extruded film, with the modifier being transferable from the film to a product surface within the casing.

A preferred thermoplastic casing is formed of extruded multilayer film including a core-barrier layer and a blend second layer adhered to the inside surface of the core layer. This second layer comprises a polyolefin first constituent and poly (ethylene oxide) second constituent of at least 70,000 average molecular weight having wood-derived liquid smoke absorbed in the blend. The color and flavor of the liquid smoke are transferable from the multilayer film to a contiguous food product receiving surface within the casing in the presence of surrounding heated water. A polyolefin third layer is adhered to the outside surface of the core layer. In a most preferred embodiment the aforedescribed thermoplastic casing is shirred.

Also contemplated is a processable food package comprising the aforedescribed extruded film as an enclosure and filled with processable food having its outer surface in fluid transfer relationship with the film enclosure inner surface. The modifier is transferable from the film enclosure to the food outer surface during processing of the food in the film enclosure.

The invention also includes a method for making a modifier-transferable film article wherein a resin blend is provided comprising said certain thermoplastic polymer and said poly (ethylene oxide). The resin blend is extruded into a film. Said certain modifier is absorbed into the blend.

Finally, the invention contemplates a method for making a modified food package wherein the aforedescribed extruded film article is provided and filled with processable food such that the food outer surface is in fluid transfer relationship with the modifier-containing film. The food-containing package is processed at elevated temperature to cook the food and simultaneously transfer the modifier from the film package to the food outer surface.

Detailed Description

The thermoplastic polymer of this invention may for example be a polyolefin, and prepared from copolymers of two or more olefins such as polyethylene and higher alpha olefins for example the C_3 to C_{10} types or copolymers of olefins and another hydrocarbon as for example ethylene-vinyl acetate (EVA), ethylene-acrylic acid (EAA), or blends thereof. The former include polypropylene, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and very low density polyethylene (VLDPE) sometimes referred to as ultra low density polyethylene (ULDPE).

Linear low density polyethylene (LLDPE) refers to copolymers of ethylene with one or more comonomers selected from preferably C_4 to C_{10} alpha-olefins such as butene-1, octene, in which long chains of copolymer are formed with relatively few side chain branches or cross-linking. The degree of branching is less than that found in typical conventional low or medium density polyethylene. LLDPE may also be characterized by the known low pressure, low temperature processes used for their production. LLDPE is known to have a density between about 0.91 and 0.93 grams per cubic centimeter and a melting point of approximately 120 °C. VLDPE is a copolymer of ethylene and at least one comonomer selected from C_4 to C_{10} alpha-olefins and having a density between about 0.86 and 0.91 g/cc and a melting point of about 120 °C.

EVA is a copolymer of ethylene and vinyl acetate, and is the preferred polyolefin as the thermoplastic polymer in the practice of this invention. For reasons explained hereinafter, the EVA more preferably has a vinyl acetate ("VA") content of between 12 and 16 wt%. This VA content may be provided by a single material or may be the weight average of at least two different EVAs having different VA contents. In particular, the polyolefin may be a blend of a first EVA having a vinyl acetate content of less than 24 wt% and a second EVA having a vinyl acetate content lower than the first EVA but more than 8 wt%. This EVA blend even more preferably comprises between 40 and 60 wt% of the first EVA and between 40 and 60 wt% of the second EVA.

For increased physical strength as for example higher puncture resistance, it may be desirable to employ a blend of different polyolefins as the thermoplastic polymer of this invention, for example a blend of ethylene-vinyl acetate and polyethylene. The latter may for example be LLDPE or VLDPE. A preferred polyolefin blend comprises EVA having between 8 wt% and 24 wt% vinyl acetate, wherein the EVA comprises between 70 wt% and 90 wt% of the blend with the polyethylene comprising between 10 wt% and 30 wt% very low density polyethylene.

The thermoplastic polymer of this invention may also for example be a polyurethane, an ionomer, a polyamide, a polyester or a vinylidene chloride copolymer (saran) as for example the vinyl chloride or methyl acrylate comonomers. These sarans function as barriers for oxygen transfer and are commonly used in food packaging for this purpose. Polyamides (nylons) and hydrolyzed ethylene-vinyl acetate (EVOH) are also oxygen barriers and may be used alone as the thermoplastic polymer in the instant film article, or as the core layer oxygen barrier in a multi layer film wherein another layer adhered thereto comprises the essential thermoplastic layer. As still another variation, the core-oxygen barrier layer may be an ethylene

vinyl alcohol-polyamide blend.

The thermoplastic polymer is present in a blend with poly (ethylene oxide) having an average molecular weight of at least 70,000; in this case the melting point and water absorptivity are in ranges particularly suitable for blending and extruding with other constituents, especially the thermoplastic polymer, thereby forming a blend which itself is an effective absorbent. The average molecular weight of the poly (ethylene oxide) is preferably about 100,000 for the same reasons.

The poly (ethylene oxide) preferably comprises at least 10 wt% of the blend because this concentration is desired to in turn assure that enough modifier is absorbed for effective transfer to the receiving surface. Most preferably the poly (ethylene oxide) comprises between 15 wt% and 40 wt% of the blend. Higher percentages are not preferred because of blending difficulties and loss of desired film properties. As a result, the physical properties of such excessively high poly (ethylene oxide) content film such as tensile strength, tear resistance and adhesion to adjacent films would tend to degrade.

In general, various conventional additives such as slip agents, anti-blocking agents and pigments can be incorporated in the film article of this invention, as is well known in the art.

A modifier is absorbed in the blend, i.e., primarily in the poly (ethylene oxide), and is transferable from the film to a receiving surface in fluid transfer relationship with the film. As used herein, "modifier" means a substance that effects a change or modification of the receiving surface to which it is transferred.

The modifier may be a colorant i.e., a substance that upon transfer, colors the receiving surface. Suitable colorants include water-soluble dyes such as the FD&C colors or lakes. The latter are pigments formed by precipitation and absorption of a dye on an insoluble base. Most commonly they are prepared from aluminum hydrate and organic dyes, i.e. the dye is absorbed on the hydrate. Suitable lakes for use as modifiers in this invention are for example obtained from Warner-Jenkinson Company, St. Louis, Missouri.

Another type of suitable modifiers are fragrances, for example vanillin, clove, orange or citric extract and 5' nucleotides such as inasine monophosphate. These substances do not necessarily impart color to the receiving surface but transfer fragrance, i.e., odor thereto.

Still another type of suitable modifiers are flavorents, i.e., substances transferring taste (not necessarily odor) to the receiving surface as for example reducing/nonreducing sugars, autolyzed yeast extracts and acidulants.

A further type of suitable modifiers are colorant-fragrances, i.e., substances which transfer both color and fragrance to the receiving surface, as for example wood-derived liquid smokes. The following is a representative list of such materials, the preferred types having a total acid content of at least 10% to assure substantial transfer of color and fragrance to the receiving surface.

Commercially Available Wood-Derived Liquid Smokes

Manufacturers Designation	Total Acid Content (e) %	Total Solid %	Absorptive Power(d)
Super Smoke (f)	15.5-16.5	25-26	1.3
Zesti Smoke Code-12 (f)	12.0	10 (about)	0.60
Royal Smoke AA (a)	11.5-12.0	10.2	0.68
Royal Smoke A (a)	10.5-11.0	9.0	0.42
Royal Smoke B (a)	8.5-9.0	8.8	0.36
Royal Smoke 16 (a)	10.0-10.5	17.6	0.62
Charsol C-12 (b)	12.0-12.5	8.3	0.54
Charsol C-10 (b)	11.5	not reported	0.40
Smokaroma Code-12 (c)	12.0	10.5	---

(a) Griffith Laboratories, Inc. 12200 South Central Ave. Alsip IL.
(b) Red Arrow Products Co., P.O. Box 507, Manitowoc, WI.
(c) Meat Industry Suppliers, Inc. 770 Frontage Rd. Northfield IL.
(d) Measured at 340 nm
(e) Also referred to as "Total Acidity"
(f) Hickory Specialities Co., Crossville, TN.

Still another type of modifier are antioxidants which are used to control rancidity of foods, as for example butylated hydroxy toluene, tocopherols and propyl gallate.

Modifiers also include antimycotic agents which are used to control mold growth in foods; these include glycerine, propylene glycol, potassium sorbate and parahydroxy benzoic acid. Other suitable modifiers include biocides such as nisin, lysozyme and enzymes.

Other types of modifiers include odor absorbents such as sodium citrate, epoxidized soy bean oil and hydrotalcite.

Another type of modifier is a surface energy modifier to achieve proper wetting of the receiving surface, as for example surfactants such as mono and diglycerides of fats and oils. These compounds may be ionic or nonionic.

The aforedescribed thermoplastic polymer-poly (ethylene oxide) blend preferably comprises one layer of a multi layer film wherein the layers are adhered to each other. The latter in turn preferably comprises at least three layers including a core oxygen barrier layer, the blend layer on one side of the barrier layer, and another layer formed of thermoplastic material on the other side of the core-oxygen barrier layer. This multilayer film is either extruded as or fabricated into a package as for example a casing or a bag capable of holding a body having an outer surface in fluid transfer relationship with the film inner surface for transfer of the modifier from the film to the body outer surface. Accordingly, the aforedescribed thermoplastic polymer-poly (ethylene oxide) blend with an absorbed modifier is the inner layer of the multilayer film.

The multilayer film of this invention embodiment can be produced by known techniques such as by coextruding the multiple layers through an annular die into a tube. If a heat shrinkable film is desired, this tube may be biaxially stretched in accordance with the conventional "double bubble" technique disclosed in US-A-3,456,044. Alternatively, the films may be fabricated by extrusion coating, wherein a base tube is extruded and succeeding layers are surface coated on the base tube in a manner such as that disclosed in the aforementioned US-A-3,741,253. Also, the multilayer film may be slot cast and biaxially stretched by tentering before the resulting sheet is fabricated into bags or casings. Still further, the inventive multilayer film may be fabricated by producing separate layers and then laminating the layers together. The present invention contemplates blown films as well as uniaxially or biaxially oriented films.

The preferred heat shrinkable multilayer film of this invention will generally have a total thickness of from 0.044 mm (1.75 mils) to 4.0 mils, and preferably of from about 2.0 mils to 0.101 mm (4.0 mils), because when the thickness of the multilayer film is more than 0.101 mm (4.0 mils), clipping problems are encountered in that it is difficult to gather together the open end of a bag made therefrom. When the thickness of the multi layer film is less than 0.044 mm (1.75 mils), the film will have diminished puncture resistance.

Although the invention will be specifically described in the form of a three layer film, in its broadest context only one layer is required. An oxygen barrier-type film, either as a single layer or as a core layer, is preferred for certain end uses as for example shrink wrapping fresh red meat or processed meat. On the other hand, oxygen barrier-type films are not normally used for shrink packaging poultry. More than three layers are also contemplated, for example, a five layer film comprising one outer layer of polypropylene or ethylene-propylene copolymer, another outer layer comprising thermoplastic polymer-poly (ethylene oxide) blend, the aforedescribed vinylidene chloride copolymer as a barrier layer and an adhesive layer between each outer layer and the barrier layer.

If the preferred three layer film is heat shrinkable for food packaging, the first outer layer will preferably have a thickness of from 0.028 mm (1.1 mils) to 0.051 mm (2.0 mils); the core layer will preferably have a thickness of from 5.1 µm (0.20 mil to) 11.4 µm (0.45 mil); and the second outer layer will preferably have a thickness of from 10.2 µm (0.4 mil) to 0.038 mm (1.5 mils). The thickness of the first outer layer, which is the inner layer of the bag, is preferably within the aforementioned range because the sealing and processability properties of the film layer would otherwise be diminished. The thickness of the core layer is preferably within the above-indicated range because the film would provide inadequate barrier properties if the core layer thickness is less than 5.1 µm (0.20 mil). The preferred upper limit of 11.4 µm (0.45 mil) for the core layer is based on the barrier effectiveness needed for intended uses of the multilayer film. The thickness of the second outer layer, which is the outer layer of the film, is preferably in the aforementioned range to provide desired toughness and puncture resistance and also keep the total thickness of the film in the range from 0.044 mm (1.75 mils) to 0.101 mm (4.0 mils).

When the vinylidene chloride copolymer is or includes the vinyl chloride copolymer and biaxial orientation is desired, the latter's molecular weight preferably is at least 75,000 to readily achieve biaxial orientation and film toughness, and up to 135,000 for ease of extrudability. The most preferred range is between 120,000 and 130,000 molecular weight. Also, the vinyl chloride content in the copolymer is preferably between 10 weight percent for ease of extrudability and up to 35 weight percent for maximum barrier properties, the most preferred range being between 15 and 30 weight percent vinyl chloride.

When the vinylidene chloride copolymer is or includes the methyl acrylate copolymer, the latter's molecular weight is preferably at least 75,000 to readily achieve the desired biaxial orientation and film toughness, and up to 130,000 for ease of extrudability. The most preferred range is between 90,000 and 110,000 molecular weight. Also, the methyl acrylate content in the copolymer is preferably between 5 weight percent for ease of extrudability and up to 15 weight percent which is the U.S. Federal Food and Drug Administration's limit. The most preferred range for methyl acrylate content is between 6 and 10 weight percent in the copolymer with vinylidene chloride.

The vinylidene chloride copolymer layer of the inventive film may also comprise a blend of two copolymers. As for example described in US-A-4,798,751, a suitable blend may be vinylidene chloride-methyl acrylate copolymer and vinylidene chloride-vinyl chloride copolymer, with between 2.9 and 13.5 weight percent methyl acrylate and between 2.9 and 11.6 weight percent vinyl chloride. This blend provides a balance between no significant discoloration on irradiation or exposure to elevated temperature for sustained periods, and avoidance of processing difficulties during manufacturing.

The vinylidene chloride copolymer core layer preferably contains less than 5 weight percent plasticizer, the percentage being based on the total weight of the blend of copolymers and all additives including plasticizer, in order to maximize the barrier properties of the thin film. Conventional plasticizers such as dibutyl sebacate and epoxidized soybean oil can be used.

To manufacture the present film article, the thermoplastic polymer and poly (ethylene oxide) are first thoroughly mixed preferably in resin form to form a substantially uniform blend. If the modifier is extrudable without decomposition or vaporization under the elevated temperature extrusion conditions, it is also intimately mixed with the other blend constituents.

The resins and any additives are introduced to an extruder (generally one extruder per layer) where the resins are melted by heating and then transferred to the coextrusion die for formation into a tube. Extruder and die temperatures will generally depend upon the particular resin or resin-containing mixtures being processed and suitable temperature ranges for commercially available resins are generally known in the art, or are provided in technical bulletins made available by resin manufacturers. Processing temperatures may vary depending upon other process parameters chosen. In coextrusion, barrel and die temperatures, for example, may range between about 175 °C and 250 °C (347 °F and 482 °F). However, depending upon the manufacturing process used and particular equipment and other process parameters utilized, variations and actual process parameters including process temperatures will be set by one skilled in the art without undue experimentation.

The entire multilayer film of this invention is preferably irradiated at dosage of at least 2 MR. If the film is biaxially oriented for heat shrinkability, the irradiation step preferably follows the biaxial orientation step. As explained in US-A-4,737,391, this post-irradiation sequence is preferred because the film to be irradiated is much thinner than the nonoriented film, so the same degree of cross-linking can be achieved at lower voltage than with the unstretched film. Using post-irradiation the multi layer film of this invention is preferably irradiated to a dosage level of between 1 megarad and 5 megarads, and most preferably between 2 megarads and 4 megarads, by any suitable method such as by employing an electron beam. When the energy level is below the indicated range, sufficient cross-linking is not obtained to improve the heat sealing characteristics and toughness properties of the multilayer film. When the energy level is above the aforementioned range, the degree of the film shrinkage is significantly reduced and further improvements in the heat sealing characteristics and toughness properties of the film are not achieved.

The modifier is absorbed into the blend either before or after film extrusion depending primarily on whether the modifier will be affected by the extrusion conditions and whether the modifier will adversely affect extrudability of the other film constituents, in particular at the high temperature on the order of 177 °C (350 °F). If it does not volatilize and/or decompose at this temperature level it may be first contacted with the poly (ethylene oxide) for absorption, and the modifier-containing poly (ethylene oxide) then blended with the thermoplastic polymer for extrusion.

If however the modifier or the other film constituents would be affected by the extrusion conditions, the modifier must be introduced to the as-formed film. If the latter is formed as a flat sheet it may be immersed in a modifier-containing bath for absorption by the poly (ethylene oxide). If the sheet is extruded as a tube, the modifier may be contacted with the tube inner surface and absorbed thereby. The most commonly used procedure for accomplishing this is by slugging as for example described in US-A-2,901,358 and US-A-3,693,583. As well understood by those skilled in the art, a slug of the modifier-containing liquid is introduced at a low position in the tube processing system, usually with at least a nip roll as a liquid seal at the lower end. A nip roll may also be provided as the upper end of the vertical flow path to prevent liquid carryover. The inflated tube is then passed through the stationery liquid slug for absorption of the modifier.

If the film is fabricated into a bag, the modifier may be added by simply filling the bag and after absorption into the film wall, draining or pressing excess modifier-containing solution from the absorptive surface.

Film packages such as bags may for example be produced from the film of this invention by heat sealing. For instance, if the film is produced in the form of tubular film, bags can be produced therefrom by heat sealing one end of a length of the tubular film or by sealing both ends of the tube, then slitting one edge to form the bag mouth. If the film of this invention is made in the form of flat sheets, bags can be formed therefrom by heat sealing three edges of two superimposed sheets of film. When carrying out the heat sealing operation, the surfaces which are heat sealed to each other to form seams are the aforedescribed inner layers of the films of the invention. Thus, for example, when forming a bag by heat sealing one edge of a length of tubular film, the inner surface of the tube, i.e., the surface which will be heat sealed to itself, will be the inner layer of the multilayer film embodiment.

For transfer of modifier from the extruded film to the contiguous receiving surface, a physical contacting relationship is preferably provided between the modifier-containing poly (ethylene oxide) and thermoplastic polymer film blend, and the receiving surface. This may for example be accomplished during the conventional shrink packaging of a heat-shrinkable film around a body as for example a processable food such as ham or poultry. Alternatively, if the film is not heat shrinkable it may be wrapped around the contiguous receiving surface as a sheet. If in bag or casing form, it may be evacuated and collapsed against the contiguous receiving surface and sealed.

There must be a driving force for transfer of the modifier from the film to the receiving surface, and this is at least in part provided by a difference in modifier concentration, i.e., concentration gradient, and by diffusion. A carrier such as water is also preferred but not essential. Modifiers such as fragrances and taste modifiers may have sufficient vapor pressure to diffuse from the film to the receiving surface without using a carrier such as water. In some systems, vapor transport of the modifier from the film to the receiving surface may be effected by surface-air-surface diffusion, thereby obviating the need for contiguous contact between the film and the receiving surface.

It will be recognized by those skilled in the art that the modifier-to-receiving surface transfer efficiency depends on a number of factors. In general, the transfer is more efficient if there is contiguous contact between the modifier-containing film and the receiving surface. Other factors include the modifier boiling point and vapor pressure, the modifier loading in the film, temperature-time relationship of the system during transfer, the modifier absorptivity of the receiving surface and the film-receiving surface distance if there is no contiguous relationship. In general, a higher transfer rate and modifier loading in the receiving surface is achieved if the modifier boiling point is relatively low, its vapor pressure is relatively high, the modifier loading in the film is relatively high, the system temperature during transfer is relatively high and maintained for a relatively long period, the receiving surface absorptivity for the modifier is relatively high, and the film-to-receiving surface flow path is relatively short and unobstructed. In preferred practice, water is present at the film-receiving surface interface as a carrier for the modifier transfer. This is usually provided by the moisture content in edible bodies if they form a receiving surface. Water is preferred as a carrier because the poly (ethylene oxide) itself is water soluble, and the modifier must be released therefrom for transfer to occur. Stated otherwise, moisture weakens the modifier-poly (ethylene oxide) bond and accelerates movement of the modifier across the film interface to the receiving surface. In some instances the modifier itself provides the water, for example wood-derived liquid smoke. If the modifier or receiving surface does not contain moisture, the latter may be provided from an external source.

The receiving surface itself is preferably a porous material such as food, to more readily receive and retain the modifier. Nonporous surfaces are difficult to penetrate in terms of transferring modifiers thereto from the poly (ethylene oxide) -thermoplastic polymer blend. Among the food bodies which have been successfully tested as receiving surfaces in the practice of the invention are the following: ham, poultry (turkey), swiss cheese and american cheese. A cardboard cylindrical core has also been successfully demonstrated as a receiving surface to simulate nonfood surfaces. If the receiving surface is contiguously associated with the film, the former should preferably be flexible so that it may be readily contoured to the film surface for good physical contact across the entire exposed surface areas.

It is preferred to effect the modifier-to-receiving surface transfer at elevated temperature, as for example during the processing of edible food such as meat and poultry inside the film package. There are at least two reasons for this preference. First, the elevated temperature increases energy and hence mobility of the water which accelerates release of the modifier from the poly (ethylene oxide). Secondly, the elevated temperature increases activity and energy of the modifier molecule itself, thereby accelerating its movement toward the receiving surface and in the direction of lowest concentration of the modifier. Notwithstanding the preference for an elevated temperature environment, it has been demonstrated that modifiers may be

transferred from the poly (ethylene oxide) across the film interface to the contiguous surface at ambient temperature.

The invention will be more fully understood by the ensuing examples.

Example 1

A series of tests were conducted to determine the liquid smoke absorbency in blown (nonoriented) monolayer films formed of ethylene-vinyl acetate. Various absorbents were added to the EVA resin to be extruded. Liquid smoke was added to the extruded film and the absorbency measured.

The liquid smoke used in this and all succeeding examples was type H-16 sold by Hickory Specialties Company and manufactured by partial oxidation of wood to produce an "as is" or tar-containing mixture having 50% water content and 16% total acid content. The EVA was type DQDA 6833 sold by Union Carbide Corporation and has a vinyl acetate content of 10 wt% and melt index of 0.25. The poly (ethylene oxide) used in these tests and all succeeding examples was Polyox® WRSN 10 manufactured by Union Carbide Corporation in powder form and having a molecular weight of 100,000, being totally water soluble (hereinafter referred to as "Polyox®"). The starch absorbent was Polygrade® II manufactured by Ampacet Chemical Company. This is a starch-linear low density polyethylene blend with a small concentration of a pro-oxidant, the starch comprising 40 wt% of the total mixture.

The experimental procedure was to immerse preweighed film swatches in a liquid smoke bath for two minutes, pat the liquid smoke sample lightly to visual dryness and reweigh, all at ambient room temperature. As used in this and all ensuing examples, the weight percent of a modifier in a film refers to the base weight of the film, i.e., without the modifier, unless stated otherwise.

The results of these absorbent screening tests are summarized in Table A.

Table A

Absorbent Screening Tests			
Sample No.	Film Composition	Liquid Smoke Absorbency (wt%)	Film Thickness* mm (mils)
1	EVA control	0.5	0.089 (3.5)
2	5% Polyox-95% EVA	1.0	0.089 (3.5)
3	10% Polyox-90% EVA	1.0	0.089 (3.5)
4	20% Polyox-80% EVA	3.9	0.15 (6.0)
5	6% starch-94% EVA	1.1	0.076 (3.0)
6	10% starch-90% EVA	1.3	0.076 (3.0)
7	5% Polyox, 6% starch, 89% EVA	2.1	0.081 (3.2)

* After liquid smoke absorption

Table A shows that if poly (ethylene oxide) is blended in sufficient quantity with EVA, the resulting film will absorb at least seven times as much liquid smoke as the same film without this particular absorbent. In particular, Sample 4 (20% Polyox®) had 3.9 wt% liquid smoke whereas Sample 1 (no Polyox®) had only 0.5% liquid smoke. In contrast, starch by itself (a well known absorbent) provided very little liquid smoke absorbency, but when blended with the Polyox® resin a much higher absorbency was obtained per Sample 7.

In these tests it was also attempted to prepare a monolayer film using a blend of EVA and Union Carbide's Polyox® WRSN 750, the latter being a poly (ethylene oxide) with a 300,000 molecular weight. Because a bubble could not be maintained, this blend could not be extruded into a film with the particular test extruder used in these experiments. It is possible that with an extruder having a longer melt flow path and more precise temperature control, blending would be more effective and a film could be formed.

Another additive tried was Nalco Chemical Company's type 1181 which is a starch based absorbent consisting of a thermoset crosslinked water soluble resin. Extrusion with EVA was unsuccessful, resulting in many film gels.

Also tested was the addition of gypsum (hydrated calcium sulfate) to the EVA resin at several different loadings. Gypsum is a well-known absorbent. However, the best results (1.1 wt% liquid smoke using 1% gypsum - 99% EVA) were far inferior to the best performing Polyox®-containing Sample 4 (3.9 wt% liquid smoke).

Example 2

Attempts were made to load more than 20% Polyox® WRSN 10 into the EVA monolayer film of the type described in Example 1. If this were possible, the liquid smoke absorbency could be increased above the 3.9 wt% of Sample 4. These attempts using the Example 1 extruder were unsuccessful because the Polyox® tended to plate out on the nip rolls of the blown film extruder.

For the foregoing reasons, other thermoplastic polymers were tested as substitutes for the EVA used in Example 1, and with the same extruder. These formulations were blended and extruded as monolayer films and immersed in the same liquid smoke for the same period as in Example 1.

The results of these tests are summarized in Table B.

Table B - Base Film Screening Tests

Sample No.	Film Composition	Liquid Smoke Absorbency (wt%)	Film Thickness mm (Mils)
8	20% Polyox®, 80% polypropylene (a)	3.7	0.084 (3.3)
9	20% Polyox®, 80% acrylic acid (b) copolymer	1.8	0.053 (2.1)
9A	20% Polyox®, 50% acrylic acid copolymer (b), 30% nylon (f)	10.0	0.051 (2.0)
10	20% Polyox®, 80% ionomer (c)	2.8	0.053 (2.1)
11	20% Polyox®, 80% VLDPE (d)	1.2	0.051 (2.0)
12	50% Polyox®, 50% VLDPE (d)	17.5	0.066 (2.6)
13	20% Polyox®, 80% EVA (18% VA) (e)	7.7	0.048 (1.9)
14	30% Polyox®, 70% EVA (18% VA)	19.1	0.056 (2.2)
14A	30% Polyox®, 35% EVA (18% VA) 35% ULDPE (d)	22.0	0.053 (2.1)
15	35% Polyox®, 65% EVA (18% VA)	22.4	0.056 (2.2)
16	40% Polyox®, 60% EVA (18% VA)	36.0	0.056 (2.2)
17	20% Polyox®, 40% EVA (10% VA) 40% EVA (18% VA) (g)	5.1	0.071 (2.8)
18	30% Polyox®, 35% EVA (10% VA) 35% EVA (18% VA)	22.9	0.071 (2.8)

The product designation and manufacturers of the Table B film components are as follows:

(a) Soltex® 4209, Soltex
(b) Primacor® 1410, (melt index = 1.5) Dow
(c) Surlyn® 8404, Du Pont
(d) Attane® 4001, Dow
(e) Elvax® 3165, DuPont
(f) W 6220, Emser Grilon
(g) DQDA 6833, Union Carbide

In another monolayer blown film test, a blend of 17% Polyox® 3% nylon (type W 6220 manufactured by Emser Grilon Company) was extruded into a flexible film of about 0,051 mm (2.0 mils) thickness and thereafter bonded with liquid smoke. The takeup was such that the film contained about 28.6% liquid smoke, thereby demonstrating that when blended with Polyox®, high modifier loading may be obtained with thermoplastic polymer other than polyolefins.

There were compatibility and mixing difficulties with certain of these blends, in particular Polyox® with polypropylene (Sample 8) and ultra low density polyethylene or ULDPE (Samples 11 and 12). The films tended to be very splitty and came apart in layers, however suitable films might be prepared from these blends with a longer extruder melt flow path and a more efficient mixing screw. The ionomer (Sample 10) and acrylic acid copolymer (Sample 9) blended well with Polyox® but did not absorb liquid smoke nearly as effectively as the EVA, 10% VA film (Sample 4). Similar results to Sample 9 were obtained with Primacor® 1470, an acrylic acid copolymer manufactured by Dow Company with relatively high melt index of 5 dg/min, i.e., the liquid smoke absorbency was only about 2 wt%.

Ethylene vinyl acetate was clearly the most effective liquid smoke absorbent among the thermoplastic materials used in these experiments. Higher absorbance values may in some instances be obtained by increasing the Polyox® content and decreasing the thermoplastic content, provided that the mixture is extrudable. This is demonstrated by comparing Examples 11 and 12.

Table B also shows that the high vinyl acetate (18%) EVA film greatly improved liquid smoke absorbency due to an ability to incorporate more Polyox®. That is, Sample 16 contained 40 wt% Polyox® hence absorbed 36.0% liquid smoke. Its Polyox® content was twice that attainable with 10% vinyl acetate EVA. However, the liquid smoke absorbency was surprisingly over nine times as much as the 20% Polyox®-80% EVA having 10% VA (Sample 4).

Since 18% VA type EVA is difficult to biaxially orient and one intended use for the film article of this invention is shrink wrapping food products such as meats, blends of this EVA with 10% VA type EVA (as used in Example 1) were also tested. Sample 18 shows that high liquid smoke absorbency may be achieved because the EVA blend contained 30% Polyox®.

The average vinyl acetate content of preferred Sample 18 was 14%. In a preferred embodiment of this invention the thermoplastic polymer is ethylene-vinyl acetate having vinyl acetate content between 12 and 16 wt%. This may be provided by blending two different EVAs with different VA contents to result in a blend having a weight averaged vinyl acetate in this range as for example demonstrated by Sample 18. Alternatively the preferred VA content may be provided by a single EVA if such is commercially available.

Example 3

Biaxially oriented, heat shrinkable multilayer films were prepared with EVA-10% vinyl acetate inner and outer layers and an oxygen barrier type core layer comprising a blend of 25 wt% vinylidene chloride-vinyl chloride copolymer with 29 wt% vinyl chloride, and 75 wt% vinylidene chloride-methyl acrylate copolymer with 8 wt% methyl acrylate. The inner layer was about 0.038 mm (1.5 mils) thick, the outer layer was about 0.017 mm (0.67 mil) thick and the core-barrier layer about 7.6 µm (0.3 mil) thick for all samples of this Example 3.

In addition to Polyox®, Sample 21 inner layer contained 10% of the aforedescribed starch absorbent Polygrade® II. Since starch comprised 40% of same, it constituted 4% by weight of the inner layer. The

additives in Samples 20 and 21 were blended with the inner layer EVA resin and the three separate layers were coextruded and thereafter biaxially oriented using the afore described double bubble process. The multilayer film samples were shaped into the form of a pouch which was weighed and then filled with the aforedescribed liquid smoke. After a contact time of about 2 minutes the excess liquid smoke was drained and the absorbate-containing inner layer was patted dry.

This Example demonstrates a preferred film embodiment of the invention comprising a biaxially oriented and heat shrinkable multilayer extruded film comprising a vinylidene chloride copolymer core-barrier layer, a blend second layer adhered to one side of the core layer, and a third layer adhered to the other side of the core layer opposite to the one side and comprising ethylene vinyl acetate. The blend second layer comprises ethylene vinyl acetate and poly (ethylene oxide) of at least 70,000 average molecular weight, with wood-derived liquid smoke absorbed by the blend after extrusion of the film. The liquid smoke color and flavor are transferable from the blend second layer to a contiguous receiving surface in the presence of water.

Before liquid smoke absorption, the samples were tested for physical properties and the results are summarized in Table C along with the smoke loading. Where two numbers are given, the first is the machine direction measurement (MD) and the second measurement (following the slash) is in the transverse direction (TD).

Table C

Multilayer Film Physical Properties[1]			
Sample No.	19	20	21
Inner Layer Composition	100% EVA control	85% EVA 15% Polyox®	86% EVA 10% Polyox® 4% Starch
Tensile Strength, (psi) MPa	40/40 (5800/5800)	46/37 (6700/5300)	39/44 (5700/6400)
Elongation, %	160/110	190/200	90/120
Shrink @ 90 °C, %	25/37	29/40	26/38
Shrink Force @ 90 °C, (gm/mil) g/µm	2.6/4.3 (65/110)	2.4/3.7 (60/95)	2.8/5.7 (70/145)
Residual Shrink Force @ Room Temperature, (gm/mil) g/µm	2.0/2.6 (50/65)	2.2/3.3 (55/85)	1.6/3.3 (40/85)
Hot H_2O Puncture, Sec.	120+	120+	5.4
Haze, %	4.5	21.4	44.2
Gloss, H.U.	79.1	49.0	48.6
Flat Width, cm (in.)	28.4 (11-3/16)	25.9 (10-13/16)	28.4 (11-3/16)
Liquid Smoke Absorption in Pouch, %	0.7	5.5	4.2

(1) Physical properties were measured before smoke absorption

Sample 20 with 15% Polyox® retained more liquid smoke than control Sample 19 or Sample 21 with 10% Polyox® and 4% starch. All of the Sample 20 physical properties were comparable to control Sample 19 except for the optical properties. Sample 20 also was more prone to delamination than control Sample 19.

To test liquid smoke transfer from these film types to meat surfaces, bags were fabricated from the multilayer films (without the aforedescribed liquid smoke absorption) and then loaded with 20% by bag weight liquid smoke (or liquid smoke blends) and heat sealed to prevent loss of the liquid. Three different solutions were used with each of the three inner layer types listed in Table C for Samples 19-21. Two of the solutions were identical and comprised only liquid smoke. The third solution was a blend of about 33% dissolved caramel, about 33% lanolin (for thickening) and the remainder liquid smoke. The 10% liquid absorption level was selected as being sufficient to achieve uniform absorption in the film inner layer inside wall, yet dryness by touch. The bags were stuffed with sweet pickled ham in sufficient quantity for contiguous contact with the multilayer film's inner layer inside surface when the film was heat shrunk around the meat's outer surface. The hams were then steam cooked in the heat-shrunk bags.

The caramel/lanolin/liquid smoke blend gave a splotchy appearance to the meat, which was considered unsuitable. Meat contacted with the liquid smoke-containing Sample 21 experienced meat adhesion

because of the starch constituent. As the film was peeled back, pieces of meat came off with the film's inner layer and exposed fresh meat surface without liquid smoke coating. For this reason the starch-containing Sample 21 was also deemed unsuitable. In contrast, all of the meat bodies contacted with the Polyox®-containing Sample 20 had a uniformly smoke colored and flavored outer surface.

This Example demonstrates a preferred processable food package of the invention wherein the thermoplastic polymer-poly (ethylene oxide) blend is one layer of a multilayer film comprising at least three layers, with the blend layer adhered to the inner surface of a core-barrier layer and having its inside surface in direct contact with the food outer surface. A polyolefin third layer adheres to the outside surface of the core layer.

Example 4

Additional multilayer films of the general type described in Example 3 were prepared by the same coextrusion-double bubble process. Sample 22 was irradiated at dosage of about 4 MR after biaxial orientation and Sample 23 was nonirradiated. In addition to 20% Polyox® in the EVA (10% VA) inner layer, Sample 22 included 1.2 wt% brown FD&C lake colorant manufactured by Warner Jenkinson Company (type 9385) in this layer. Lakes are pigments formed by precipitation and absorption of a dye (in this instance brown) on an insoluble base (in this instance aluminum hydrate). The brown lake was blended with the EVA-Polyox® mixture and the film samples were a tinted bronze color. Sample 23 had an inner layer comprising 35% EVA (10% vinyl acetate), 35% EVA (18% vinyl acetate) and 30% Polyox®.

Their physical properties were measured and are summarized in Table D.

Table D

Lake-Containing Multilayer Film Physical Properties		
Sample No.	22	23
Irradiated @ 4 MR	Yes	No
Film Thickness, mm (mils)	0.059 (2.31)	0.050 (1.97)
Shrinkage @ 90 °C, %	23/28	36/41
Shrink Force @ 90 °C, g/µm (g/mil)	43/47 (110/120)	-
Residual Shrink Force, g/µm (g/mil) @ Room Temperature	3.2/4.1 (80/105)	-
Hot H_2O Puncture, sec.	120+	-
Haze, %	-	64
Gloss, Hunter Units	-	35

Example 5

Bags were formed from the biaxially oriented, heat shrinkable and irradiated Sample 22 multilayer film having an EVA layer containing 20% Polyox® and 1.2% brown tint. One group of these bags was loaded with the aforedescribed liquid smoke at a level of 20% of the bag total weight. This was done in the aforedescribed manner, i.e., filling the bag with liquid and then draining excess liquid. Another group of the same Sample 22 bags was loaded to the same 20% bag total weight level with a 50/50 mixture of liquid smoke and methyl glyoxal. These are Samples 25-27.

The Sample 23 film-type bag was loaded in the same manner to a level of 40% bag ("high level") weight with liquid smoke and without tint (Sample 28). Other Sample 23-type bags were loaded in the same manner with a 50/50 mixture of liquid smoke and methyl glyoxal(Sample 29) to the same 40% bag weight.

The aforedescribed untinted, brown tinted, liquid smoke and liquid smoke-methyl glyoxal treated bags were hand stuffed with chunk ham, and then cooked in situ in a steam atmosphere to determine the transfer of color and flavor to the cooked ham outer surfaces. The cooking conditions were 63 °C (145 °F) for 1 hour, 68 °C (155 °F) for 1 1/2 hours, and at 82 °C (180 °F) until a final internal temperature of 68 °C (155 °F) was reached. The cooked ham outer surfaces were examined and the results are summarized in Table E.

Table E

Use of Tinted Film	
Sample No. and Film Inner Layer	Appearance of Cooked Ham Surface
24 - clear, no smoke	no color change
25 - tinted, no smoke	slight purple-red tint
26 - tinted, smoke	slight purple-red tint to smoke color, splotchy and uneven
27 - tinted, smoke and methyl glyoxal	slight purple-red tint to smoke color, darker than Sample 26, somewhat splotchy and uneven
28 - clear, high level smoke	good smoked color
29 - clear, smoke and methyl glyoxal	good smoked color although somewhat splotchy

After cooking, the outside color of the tinted bags i.e., Samples 24-27 with brown lake in the inner layer, were a plum color with a copper sheen. The outside color of clear bags with liquid smoke treatment, i.e., Samples 28 and 29, was a silvery gold. These samples also delaminated in areas and were very pliable. Liquid smoke appeared to accumulate in some of the delaminated areas of Samples 28 and 29. There were small droplets of liquid smoke on the inside surfaces of Samples 26 and 27. Based on visual comparison of the cooked ham outer surfaces, Sample 28 (Sample 23 film with high level liquid smoke loading) provided the most desirable smoke color and flavor.

This Example demonstrates preparation of an embodiment of the invention comprising a thermoplastic bag formed of extruded multi layer film. The latter includes a core-barrier layer, a blend second layer adhered to the inside surface of the core layer, and a polyolefin third layer adhered to the outside surface of the core layer. The aforementioned blend second layer comprises a polyolefin first constituent and a poly (ethylene oxide) second constituent of at least 70,000 average molecular weight, wood-derived liquid smoke absorbed in the blend with the color and flavor of the liquid smoke being transferable from the multilayer films to a contiguous food product receiving surface within the bag in the presence of surrounding heated water.

Example 6

A series of tests were conducted to demonstrate that the film article of this invention may be used to transfer colorant to poultry, and also compare the performance of same with a commercially available film, W. R. Grace's type CN 590 which is a multilayer type having a polypropylene inner layer.

The inventive film article used in these tests was the multilayer Sample 18 type wherein the inner layer comprised 30% Polyox®, 35% EVA (10% VA) and 35% EVA (18% VA). Both the film article and the commercially available film were loaded in bag form with liquid smoke to provide an article containing about 28.6% liquid (total weight basis).

Liquid smoke was transferred to turkey by three different procedures: (1) the uncooked poultry was stuffed into the liquid smoke-containing bags which were evacuated, sealed and steam cooked, (2) cooked poultry breast roll was stuffed in the same type bags and steam heated at 82 °C (180 °F) for 10 minutes to simulate pasteurization, and (3) cooked poultry breast roll was stuffed in the same type bags and passed through a shrink tunnel at 91 °C (195 °F).

The turkey processed by procedure (1) in the inventive film article had even and dark smoke color with strong smoke flavor. The identically processed turkey from the commercially available film had some areas of dark smoke color and other areas of poor color. This was because the commercially available film lacked Polyox® so relatively little liquid smoke was absorbed and that available was not evenly distributed in or on the film. As a result it was not uniformly transferred to the turkey outer surface. The turkey processed by procedure (2) in the inventive film article also had even and dark smoke color with strong smoke flavor whereas the identically processed turkey from the commercially available film had uneven smoke color and flavor. The turkey processed by procedure (3) in general had less smoke color and flavor than that processed by procedure (2) because the smoke-poultry contact time at elevated temperature was much shorter. It was also observed that a large portion of the liquid smoke was still absorbed in the procedure (3) film's Polyox®, indicating that longer contact time at elevated temperature is needed for more effective transfer. Nevertheless the turkey processed in the inventive film article by procedure (3) had more pronounced smoke color and flavor than that processed in the commercially available film article.

Example 7

This series of tests demonstrates that the inventive film article may be used to transfer color to food products other than meat or poultry, and for that matter to any type of porous body. The tests also demonstrate that at least for some porous bodies the transfer may be effected at low temperature. The film article used for these tests was the same type used in Example 6, the Sample 18 multi layer biaxially oriented and heat shrinkable film with an EVA inner layer containing Polyox® and 28.6% by weight liquid smoke. The liquid smoke was added to the films by slugging. In each instance the porous body was inserted in a bag formed from the film article, the package was evacuated and shrunk at 90°C for 5 seconds. The packages were stored at 4°C (40°F) for 24 hours prior to evaluation.

For Sample 30 the porous surface was swiss cheese, and for Sample 31 the porous surface was American cheese. For Sample 32 the porous surface was a cardboard cylindrical core. The results of these tests are summarized in Table F.

Table F

Cheese and Cardboard Transfer		
Sample No.	Recipient Body	Visual Result
30	Swiss Cheese	good color/flavor transfer; slight splotchy appearance
31	American Cheese	good color/flavor transfer; slight splotchy appearance
32	Cardboard Core	good color/flavor transfer

Example 8

This series of tests was conducted to demonstrate manufacture of the inventive film article on full scale commercial equipment and at commercial production rates.

The film was a multi layer type comprising a 70.6% VLDPE, 25% EVA (18% VA) 4.4% processing aid concentrate outer layer [20 µm (0.8 mils) thick], a vinylidene chloride-methyl acrylate copolymer, vinylidene chloride-vinyl chloride copolymer blend core-barrier layer [7.6 µm (0.3 mils) thick] and an inner layer comprising a blend of 35% EVA-10% vinyl acetate, 35% EVA-18% vinyl acetate and 30% Polyox® [43 µm (1.7 mils) thick]. The film was coextruded and then biaxially oriented by the double bubble procedure into 24.1 cm (9 1/2 inch) width tubes.

The modifiers used in these tests were the aforedescribed type H-16, and Charsol® C-12 manufactured by Red Arrow Products Co. having a total acid content of 12.0-12.5%. Thus, Charsol® C-12 is not as concentrated as liquid smoke type H-16 having an acid content of about 16%, dispersed in water.

The liquid smoke was absorbed into the Polox®-containing film inner layer by drawing the tube through an internal slug of the liquid at rates of 300 m/min (1000 fpm) and 150 m/min (500 fpm). As understood by those skilled in the art, when slugging speed increases viscous drag forces also increase and this increases the rate of liquid smoke pickup. For example, at tube draw rate of 300 m/min (1000 fpm) the liquid smoke pickup was 33.6 wt%. However, excess liquid smoke was visible throughout the film inner layer and when the excess was wiped off, about 26.9 wt% liquid smoke remained. At the lower draw rate of 150 m/min (500 fpm), the liquid smoke absorbency was 27% and after wiping with a cloth the liquid smoke loading was 26.2 wt%. The H-16 treated casings had a dark amber color and the Charsol® C-12 treated casings had a bright straw color.

Because of the excess liquid smoke, there were strips of dark brown colored liquid smoke along the outer edges of the casings. These were in part due to the creases at the tube outer edges.

These liquid smoke treated casings were stuffed with chunk and form turkey (10 wt% moisture) and ham (40 wt% moisture). After being closed at the ends by clipping, the food packages were cooked in a steam atmosphere using the following heating program: 66°C (150°F) for 1 hour, 71°C (160°F) for 1 hour and 77°C (170°F) until the internal temperature of the meat reached 71°C (160°F). Then the food packages were showered with water at about 13°C (55°F) for 45 minutes.

The H-16 liquid smoke treated meat samples were dark and had a pleasantly strong smoke odor. All meat samples had the aforementioned dark strips transferred from the casing creases. The ham samples had a high level of "purge" water accumulating between the meat outer surface and the film. The turkey samples also had stripes and wrinkle dark lines, but little purge. There was no adhesion between the film

and either the turkey or ham surfaces using H-16 liquid smoke.

The C-12 liquid smoke-contacted turkey and ham samples had a pleasant smoke odor and a slight color transfer compared to the control samples cooked in the same type of bag without liquid smoke absorption. Purge water was less than with the H-16 liquid smoke samples. There was good adhesion between both types of meat surfaces and the film using C-12 liquid smoke, although considerably greater for ham than turkey.

Example 9

This test was conducted to demonstrate that as long as an environment for fluid transfer relationship exists, the modifier may be transferred to a receiving surface which is not in contiguous, i.e., physical contacting relationship with the modifier-containing film

The film was the same multilayer coextruded type used in Example 8 having an inner layer comprising a blend of 35% EVA (10% VA), 35% EVA (18% VA) and 35% Polyox®. The modifier was liquid smoke type H-16 introduced by slugging, and comprised about 26.9% of the film total weight.

Hot water cooked turkey breast slices of about 3.2 mm (1/8 inch) thickness were placed in the bottom of a beaker having a volume of 100 ml and a diameter of 10 cm (4 inches). The beaker mouth [80.6 cm^2 (12.5 in^2) surface] was covered by a small piece of the aforedescribed film with the inner layer on the underside facing the meat. The film-covered, turkey-containing beaker was placed in an oxygen barrier type heat shrinkable multilayer film bag to comprise a package, and cooked at 71 °C (160 °F) for 1 hour. The package was then placed in a refrigerator maintained at 4 °C (40 °F), and kept there for 48 hours.

At the end of the refrigeration period the turkey slices were removed for visual inspection, tasting and odor detection. There was a distinct smoke odor in the turkey slices as well as a smoke flavor. Because of the fluid transfer relationship therebetween, the liquid smoke modifier had transferred from the film to the turkey slices without direct physical contact. In this instance the liquid smoke modifier was released from the thermoplastic polymer-Polyox® blend by heating the package and the resulting smoke vapor permeated the turkey slices.

Example 10

This test was conducted to demonstrate that the modifier may be transferred to a receiving surface in the absence of water.

A blown (nonoriented) monolayer film was extruded having the following content: 30% EVA (10% VA), 30% EVA (18% VA), 30% Polyox® and 10% AFT P 1138 smoke concentrate. The latter is a 30% smoke-in-oil flavor in polyolefin composition obtained from Applied Fragrance Technologies, Inc. Accordingly, there was no moisture in this film which had a thickness of about 79 µm (3.1 mils).

A white ceramic tile was wrapped with this film to form a package and the latter was placed in a bag formed of heat shrinkable oxygen barrier layer-type multilayer film. The bag was evacuated, sealed and shrunk at 90 °C for 5 seconds. After room temperature storage for 48 hours, the package was recovered and the tile examined. The tile had a distinct smoke odor and slight yellow color, thereby demonstrating transfer of the modifier smoke to the ceramic receiving surface in the absence of moisture.

Claims

1. An extruded film article comprising a blend of (i) a thermoplastic polymer selected from polyolefins, polyurethanes, ionomers, polyamides, polyesters, vinylidene chloride copolymers and hydrolyzed ethylene-vinyl acetate-copolymers, (ii) poly(ethylene oxide) having an average molecular weight of at least 70,000 and (iii) a modifier selected from colorants, fragrances, flavorents, colorant-fragrances, antioxidants for controlling the rancidity of foods, antimycotic agents, biocides, odor absorbents and surface energy modifiers, said modifier being absorbed in said blend and being transferable from said film to a receiving surface in fluid transfer relationship with said film.

2. An article according to claim 1 wherein said thermoplastic polymer is polyolefin, e.g. ethylene-vinyl acetate (EVA) which preferably has a vinyl acetate content of between 12 and 16 wt%.

3. An article according to claim 2 wherein said polyolefin comprises a blend of a first EVA having a vinyl acetate content of less than 24 wt% and a second EVA having a vinyl acetate content lower than said first EVA but more than 8 wt%.

4. An article according to claim 3, wherein the polyolefin blend comprises between 40 and 60 wt% of said first EVA, and between 40 and 60 wt% of said second EVA.

5. An article according to at least one of the claims 1 to 4, wherein said polyolefin is a blend of EVA and polyethylene, e.g. linear low density polyethylene or very low density polyethylene.

6. An article according to claim 5, wherein said EVA has between 8 wt% and 24 wt% vinyl acetate, said EVA comprises between 70 wt% and 90 wt% of said blend, and said polyethylene comprises between 10 wt% and 30 wt% very low density polyethylene.

7. An article according to claim 1, wherein said thermoplastic polymer is polyamide.

8. An article according to at least one of the claims 1 to 7, wherein said poly (ethylene oxide) has an average molecular weight of about 100,000.

9. An article according to at least one of the claims 1 to 8, wherein said poly(ethylene oxide) comprises at least 10 wt% of said blend, e.g. between 15 wt% and 40 wt% of said blend.

10. An article according to at least one of the claims 1 to 9, wherein said modifier is absorbed by said blend after extrusion of said film.

11. An article according to at least one of the claims 1 to 10, wherein said modifier is a colorant, a fragrance, a colorant-fragrance or a biocide.

12. An article according to claim 11, wherein said colorant-fragrance is wood-derived liquid smoke.

13. An article according to claim 12, wherein said liquid smoke has a total acid content of at least 10%.

14. An article according to at least one of the claims 12 and 13, wherein said liquid smoke comprises between 10 wt% and 40 wt% of said article.

15. An article according to at least one of the claims 1 to 14, wherein said blend comprises one layer of a multilayer film.

16. An article according to claim 15, wherein said multilayer film comprises at least three layers including a core-oxygen barrier layer, the blend layer on one side of said barrier layer, and another layer formed of thermoplastic material on the other side of said core-oxygen barrier layer, with said modifier being transferable from said blend layer to said receiving surface in fluid transfer relationship with said blend layer.

17. A multilayer film according to claim 16, wherein said core-oxygen barrier layer is a vinylidene chloride copolymer.

18. A multilayer film according to claim 16, wherein said core-oxygen barrier layer is ethylene-vinyl alcohol or an ethylene-vinyl alcohol-polyamide blend.

19. A multilayer film acording to at least one of the claims 16 to 18, wherein said thermoplastic polymer in said blend layer is polyolefin.

20. A multilayer film acording to at least one of the claims 16 to 19, wherein said thermoplastic polymer in said blend layer and said other layer are formed of polyolefin.

21. A multilayer film according to at least one of the claims 16 to 20 which is biaxially oriented and heat shrinkable.

22. A biaxially oriented and heat shrinkable multilayer extruded film comprising a vinylidene chloride copolymer core-barrier layer; a blend second layer adhered to one side of the core layer and comprising components (i) to (iii) as defined in claim 1 wherein component (i) is a polyolefin, said

modifier (iii) being transferable from said blend second layer of the multilayer film to a contiguous receiving surface in the presence of water; and a polyolefin third layer adhered to the other side of said core layer opposite to said one side.

23. A multilayer film according to claim 22, wherein said polyolefin of both said second and third layers is ethylene-vinyl acetate, and said modifier is wood-derived liquid smoke absorbed by said blend after extrusion of said film with the liquid smoke color and flavor being transferable to said contiguous surface.

24. A multilayer film according to at least one of the claims 16 to 23 which is irradiated at a dosage of at least 2 MR.

25. A thermoplastic bag formed of an extruded film according to claim 1, said modifier (iii) being transferable from said film to a product receiving surface within said bag.

26. A thermoplastic bag formed of extruded mulilayer film comprising a core-barrier layer; a blend second layer adhered to the inside surface of the core layer and comprising a polyolefin first constituent and a poly(ethylene oxide) second constituent of at least 70,000 average molecular weight, wood-derived liquid smoke absorbed in said blend with the color and flavor of said liquid smoke being transferable from said multilayer film to a contiguous food product receiving surface within said bag in the presence of heated water; and a polyolefin third layer adhered to the outside surface of the core layer.

27. A thermoplastic bag according to at least one of the claims 25 and 26, wherein the multilayer film is irradiated at dosage of at least 2 MR.

28. A thermoplastic casing formed of an extruded film according to claim 1, said modifier (iii) being transferable from said film to a product surface within said casing.

29. A thermoplastic casing formed of extruded multilayer film comprising a core-barrier layer; a blend second layer adhered to the inside surface of the core layer and comprising a polyolefin first constituent and a poly(ethylene oxide) second constituent of at least 70,000 average molecular weight having wood-derived liquid smoke absorbed in said blend with the color and flavor of said liquid smoke being transferable from said multilayer film to a contiguous food product receiving surface within said casing in the presence of heated water; and a polyolefin third layer adhered to the outside surface of said core layer.

30. A casing according to at least one of the claims 28 and 29 which is shirred.

31. A thermoplastic casing according to at least one of the claims 29 and 30, wherein the multilayer film is irradiated at a dosage of at least 2 MR.

32. A processable food package comprising an extruded thermoplastic film enclosure filled with processable food having its outer surface in fluid transfer relationship with the film enclosure inner surface, said film enclosure comprising the blend of components (i) to (iii) as defined in claim 1 and said modifier (iii) being transferable from said film enclosure to the food outer surface during processing thereof in said film enclosure.

33. A processable food package according to claim 32, wherein said processable food is moisture-containing and its outer surface is in contiguous contact with the film enclosure inner surface.

34. A processable food package according to at least one of the claims 32 and 33, wherein said thermoplastic polymer (i) is ethylene-vinyl acetate having a vinyl acetate content between 12 and 16 wt%.

35. A processable food package according to at least one of the claims 32 and 34, wherein said modifier (iii) is wood-derived liquid smoke whose color and flavor are transferable to the food outer surface during processing thereof in said food enclosure.

36. A processable food package according to at least one of the claims 32 to 34, wherein said modifier (iii) is a colorant whose color is transferable to the food outer surface during processing thereof in said food enclosure.

37. A processable food package according to at least one of the claims 32 to 36, wherein said blend is one layer of a multilayer film comprising at least three layers including a core-barrier layer, the blend layer being adhered to the inner surface of said core layer with its inside surface in direct contact with said food outer surface, and a polyolefin third layer adhered to the outside surface of said core layer, said multilayer film may be irradiated at a dosage of at least 2 MR.

38. A method for making a modifier transferable film article comprising the steps of:
a) providing a resin blend comprising (i) a thermoplastic polymer selected from polyolefins, polyurethanes, ionomers, polyamides, polyesters, vinylidene chloride copolymers and hydrolyzed ethylene-vinyl acetate-copolymers and (ii) a poly(ethylene oxide) having an average molecular weight of at least 70,000,
b) extruding said resin blend into a film, and
c) absorbing (iii) a modifier as defined in claim 1 into the extruded blend.

39. A method according to claim 38, wherein said poly(ethylene oxide) has an average molecular weight of about 100,000.

40. A method according to at least one of the claims 38 and 39, wherein said thermoplastic polymer is polyolefin, preferably ethylene-vinyl acetate (EVA) having a vinyl acetate content of preferably between 12 and 16 wt%.

41. A method according to claim 40, wherein said polyolefin comprises a blend of a first EVA having a vinyl acetate content of less than 24 wt% and a second EVA having a vinyl acetate content of more than 8 wt%.

42. A method according to claim 40, wherein said polyolefin is a blend of EVA and polyethylene, e.g. linear low density or very low density polyethylene.

43. A method according to at least one of the claims 38 and 39, wherein said thermoplastic polymer is polyamide.

44. A method according to at least one of the claims 38 to 43, wherein the extruded film is biaxially oriented.

45. A method according to at least one of the claims 38 to 44, wherein an oxygen barrier resin and a thermoplastic resin are provided and separately extruded along with said resin blend to form a three layer film comprising an oxygen barrier layer, the blend as a second layer adhered to said oxygen barrier layer on one side thereof, and the thermoplastic resin as a third layer adhered to said oxygen barrier layer on the other side thereof opposite from the blend layer.

46. A method according to claim 45, wherein the extruded three layer film is biaxially oriented.

47. A method according to claim 45, wherein the extruded film is irradiated at a dosage of at least 2 MR.

48. A method according to at least one of the claims 38 to 47, wherein said modifier is a colorant, a fragrance, a colorant-fragrance, e.g. wood-derived liquid smoke, or a biocide.

49. A method for making a modified food package comprising the steps of:
a) providing an extruded film article having walls comprising the blend of components (i) to (iii) as defined in claim 1, said modifier (iii) being absorbed in said blend;
b) filling said film article with processable food such that the food outer surface is in fluid transfer relationship with the modifier-containing film;
c) processing the food-containing package at elevated temperature in the presence of surrounding heated water to cook said food and simultaneously transfer said modifier from said film package to

the water processed food outer surface.

50. A method according to claim 49, wherein said processable food is moisture-containing and its outer surface is in contiguous contact with the modifier-containing film.

51. A method according to at least one of the claims 49 and 50, wherein said thermoplastic polymer (i) is polyolefin, preferably ethylene-vinyl acetate (EVA) having an vinyl acetate content of preferably between 12 and 16 wt%.

52. A method according to at least one of the claims 49 and 51, wherein said polyolefin comprises a blend of a first EVA having a vinyl acetate content of less than 24 wt% and a second EVA having a vinyl acetate content lower than said first EVA but more than 8 wt%.

53. A method according to claim 51, wherein said polyolefin is a blend of EVA and polyethylene, e.g. linear low density polyethylene or very low density polyethylene.

54. A method according to at least one of the claims 49 and 50, wherein said thermoplastic polymer is polyamide.

55. A method according to at least one of the claims 49 to 54, wherein the extruded film is biaxially oriented.

56. A method according to at least one of the claims 49 to 55, wherein said modifier is a colorant or a colorant-fragrance, e.g. wood-derived liquid smoke.

57. A method according to claim 56, wherein smoke color and flavor are transferred to the food outer surface during said processing at high temperature.

58. A method according to at least one of the claims 49 to 57, wherein said film package comprises a multilayer film including a core-oxygen barrier layer, the blend layer being adhered to the oxygen barrier layer on the inside surface thereof for said direct contact with the food outer surface, and another layer formed of thermoplastic material adhered to the oxygen barrier layer on the outside surface thereof, said multilayer film bag irradiated at a dosage of at least 2 MR.

59. A method according to claim 58, wherein said component (i) of the blend is EVA having a vinyl acetate content of between 12 and 16 wt%, said oxygen barrier layer is a vinylidene chloride copolymer, said thermoplastic layer is a polyolefin, said modifier is wood-derived liquid smoke, and smoke color and flavor are transferred to the food outer surface during said processing at high temperature.

Patentansprüche

1. Stranggepreßtes Folienprodukt, welches umfaßt: eine Mischung aus (i) einem thermoplastischen Polymer, ausgewählt aus Polyolefinen, Polyurethanen, lonomeren, Polyamiden, Polyestern, Vinylidenchlorid-Copolymeren und hydrolysierten Ethylen-Vinylacetat-Copolymeren, (ii) Poly(ethylenoxid) mit einem durchschnittlichen Molekulargewicht von wenigstens 70.000 und (iii) ein Modifizierungsmittel, ausgewählt aus Färbemitteln, Aromen, Geschmacksstoffen, farbgebenden Aromen, Antioxidationsmitteln zur Bekämpfung von Ranzigkeit von Nahrungsmitteln, Mittel gegen Pilzbefall, Bioziden, Geruchsabsorptionsmitteln und Modifizierungsmitteln der Oberflächenenergie, wobei das genannte Modifizierungsmittel von der genannten Mischung absorbiert und von der genannten Folie auf eine Empfängeroberfläche durch Fliudtransfer aus der genannten Folie übertragbar ist.

2. Gegenstand nach Anspruch 1, worin das genannte thermoplastische Polymer Polyolefin ist, z. B. Ethylen-Vinylacetat (EVA) mit einem Vinylacetatgehalt von vorzugsweise zwischen 12 und 16 Gew.-%.

3. Gegenstand nach Anspruch 2, worin das genannte Polyolefin eine Mischung eines ersten EVA mit einem Vinylacetatgehalt von weniger als 24 Gew.-% und einem zweiten EVA mit einem Vinylacetatgehalt von weniger als dem des ersten EVA jedoch von mehr als 8 Gew.-% umfaßt.

4. Gegenstand nach Anspruch 3, worin die Polyolefinmischung zwischen 40 und 60 Gew.-% des genannten ersten EVA und zwischen 40 und 60 Gew.-% des genannten zweiten EVA umfaßt.

5. Gegenstand nach wenigstens einem der Ansprüche 1 bis 4, wobei das genannte Polyolefin eine Mischung von EVA und Polyethylen, z. B. einem linearen Polyethylen mit geringer Dichte oder einem Polyethylen mit sehr geringer Dichte ist.

6. Gegenstand nach Anspruch 5, worin das genannte EVA zwischen 8 Gew.-% und 24 Gew.-% Vinylacetat enthält, das genannte EVA zwischen 70 Gew.-% und 90 Gew.-% der genannten Mischung umfaßt und das genannte Polyethylen zwischen 10 Gew.-% und 30 Gew.-% Polyethylen mit sehr geringer Dichte umfaßt.

7. Gegenstand nach Anspruch 1, worin das genannte thermoplastische Polymer Polyamid ist.

8. Gegenstand nach wenigstens einem der Ansprüche 1 bis 7, worin das genannte Poly(ethylenoxid) ein durchschnittliches Molekulargewicht von etwa 100.000 aufweist.

9. Gegenstand nach wenigstens einem der Ansprüche 1 bis 8, worin das genannte Poly(ethylenoxid) wenigstens 10 Gew.-% der genannten Mischung, z. B. zwischen 15 Gew.-% und 40 Gew.-% der genannten Mischung, umfaßt.

10. Gegenstand nach wenigstens einem der Ansprüche 1 bis 9, worin das genannte Modifizierungsmittel von der genannten Mischung nach dem Strangpressen der genannten Folie absorbiert wird.

11. Gegenstand nach wenigstens einem der Ansprüche 1 bis 10, worin das genannte Modifizierungsmittel ein Färbemittel, ein Aromastoff, ein farbgebender Aromastoff oder ein Biozid ist.

12. Gegenstand nach Anspruch 11, worin der genannte farbgebende Aromastoff ein Flüssig-Rauch ist, der von Holz stammt.

13. Gegenstand nach Anspruch 12, worin der genannte Flüssig-Rauch einen Gesamtsäuregehalt von wenigstens 10% hat.

14. Gegenstand nach wenigstens einem der Ansprüche 12 und 13, worin der genannte Flüssig-Rauch zwischen 10 Gew.-% und 40 Gew.-% des genannten Gegenstands umfaßt.

15. Gegenstand nach wenigstens einem der Ansprüche 1 bis 14, worin die genannte Mischung eine Schicht einer mehrschichtigen Folie umfaßt.

16. Gegenstand nach Anspruch 15, worin die genannte mehrschichtige Folie wenigstens drei Schichten einschließlich einer Kern-Sauerstoff-Sperrschicht (Innenschicht) umfaßt: die Mischungsschicht auf der einen Seite der genannten Sperrschicht, und eine andere Schicht aus thermoplastischem Material auf der anderen Seite der genannten Kern-Sauerstoff-Sperrschicht, wobei das genannte Modifizierungsmittel von der genannten Mischungsschicht auf die Empfängeroberfläche durch Fluidtransfer aus der genannten Mischungsschicht übertragbar ist.

17. Mehrschichtige Folie nach Anspruch 16, worin die genannte Kern-Sauerstoffsperrschicht ein Vinylidenchlorid-Copolymer ist.

18. Mehrschichtige Folie nach Anspruch 16, worin die genannte Kern-Sauerstoffsperrschicht ein Ethylen-Vinylalkohol oder eine Ethylen-Vinylalkohol-Polyamid-Mischung ist.

19. Mehrschichtige Folie nach wenigstens einem der Ansprüche 16 bis 18, worin das genannte thermoplastische Polymer in der genannten Mischungsschicht Polyolefin ist.

20. Mehrschichtige Folie nach wenigstens einem der Ansprüche 16 bis 19, worin das genannte thermoplastische Polymer in der genannten Mischungsschicht und die genannte andere Schicht aus Polyolefin gebildet wird.

21. Mehrschichtige Folie nach wenigstens einem der Ansprüche 16 bis 20, die biaxial orientiert und hitzeschrumpfbar ist.

22. Biaxial orientierte und hitzeschrumpfbare mehrschichtige stranggepreßte Folie, die umfaßt: eine Vinylidenchlorid-Copolymer-Kern-Sperrschicht; eine zweite Mischungsschicht, die an einer Seite der Kernschicht haftet und die Komponenten (i) bis (iii) nach Anspruch 1 umfaßt, worin die Komponente (i) ein Polyolefin ist, das genannte Modifizierungsmittel (iii) von der genannten zweiten Mischungsschicht der mehrschichtigen Folie auf eine angrenzende Empfängeroberfläche in Anwesenheit von Wasser übertragbar ist; und eine dritte Polyolefinschicht, die an der anderen Seite der genannten Kernschicht gegenüber der genannten einen Seite haftet.

23. Mehrschichtige Folie nach Anspruch 22, worin das genannte Polyolefin der beiden genannten zweiten und dritten Schichten Ethylen-Vinylacetat ist, und das genannte Modifizierungsmittel ein Flüssig-Rauch ist, der von Holz stammt und von der genannten Mischung nach dem Strangpressen der genannten Folie mit der Farbe des Flüssig-Rauchs und des Aromas auf die genannte angrenzende Oberfläche übertragbar ist.

24. Mehrschichtige Folie nach wenigstens einem der Ansprüche 16 bis 23, die in Dosierungen von wenigstens 2 MR bestrahlt ist.

25. Thermoplastische Tasche, gebildet aus einer stranggepreßten Folie nach Anspruch 1, wobei das genannte Modifizierungsmittel (iii) aus der genannten Folie auf eine Empfängeroberfläche eines Produkts in der genannten Tasche übertragbar ist.

26. Thermoplastische Tasche bzw. Beutel, gebildet aus einer stranggepreßten mehrschichtigen Folie, die umfaßt: eine Kern-Sperrschicht, eine zweite Mischungsschicht, die an der Innenseite der Kernschicht haftet und als ersten Bestandteil ein Polyolefin und als zweiten Bestandteil ein Poly(ethylenoxid) mit einem durchschnittlichen Molekulargewicht von wenigstens 70.000 umfaßt, wobei von Holz stammender Flüssig-Rauch in der genannten Mischung absorbiert ist und wobei die Farbe und das Aroma des genannten Flüssig-Rauchs von der mehrschichtigen Folie auf eine benachbarte Empfängeroberfläche eines Lebensmittelprodukts in der genannten Tasche in Anwesenheit von erhitztem Wasser übertragbar ist; und eine dritte Polyolefinschicht, die an der Außenseite der genannten Kernschicht haftet.

27. Thermoplastische Tasche nach wenigstens einem der Ansprüche 25 und 26, worin die mehrschichtige Folie mit einer Dosis von wenigstens 2 MR bestrahlt ist.

28. Thermoplastische Hülle, die aus einer stranggepreßten Folie nach Anspruch 1 gebildet wurde, wobei das genannte Modifizierungsmittel (iii) von der genannten Folie auf die Produktoberfläche in der genannten Hülle übertragbar ist.

29. Thermoplastische Hülle, gebildet aus einer stranggepreßten mehrschichtigen Folie, die umfaßt: eine Kern-Sperrschicht, eine zweite Mischungsschicht, die an der inneren Oberfläche der Kernschicht haftet und als ersten Bestandteil ein Polyolefin und als zweiten Bestandteil ein Poly(ethylenoxid) mit einem durchschnittlichen Molekulargewicht von wenigstens 70.000 umfaßt, wobei von Holz stammender Flüsssig-Rauch in der genannten Mischung absorbiert ist und wobei die Farbe und das Aroma des genannten Flüssig-Rauchs von der mehrschichtigen Folie auf eine benachbarte Empfängeroberfläche eines Lebensmittelprodukts in der genannten Hülle in Anwesenheit von erhitztem Wasser übertragbar ist; und eine dritte Polyolefinschicht, die an der äußeren Oberfläche der genannten Kernschicht haftet.

30. Hülle nach wenigstens einem der Ansprüche 28 und 29, die gefältelt ist.

31. Thermoplastische Hülle nach wenigstens einem der Ansprüche 29 und 30, worin die mehrschichtige Folie mit einer Dosis von wenigstens 2 MR bestrahlt ist.

32. Verarbeitbare Lebensmittelunterbringung, die eine stranggepreßte thermoplastische Folienhülle, die mit einem verarbeitbaren Lebensmittel gefüllt ist, umfaßt, wobei die Möglichkeit eines Fluidtransfers von der inneren Oberfläche der Folienhülle zu der äußeren Oberfläche des Lebensmittels besteht, und die genannte Folienhülle die Mischung der Komponenten (i) bis (iii) nach Anspruch 1 umfaßt, und wobei

das genannte Modifizierungsmittel (iii) von der genannten Folienhülle zu der äußeren Oberfläche des Lebensmittels während dessen Verarbeitung in der genannten Folienhülle übertragbar ist.

33. Verarbeitbare Lebensmittelunterbringung nach Anspruch 32, worin das genannte verarbeitbare Lebensmittel Feuchtigkeit enthält und dessen äußere Oberfläche sich in angrenzendem Kontakt mit der inneren Oberfläche der Folienhülle befindet.

34. Verarbeitbare Lebensmittelunterbringung nach wenigstens einem der Ansprüche 32 und 33, worin das genannte thermoplastische Polymer (i) Ethylen-Vinylacetat mit einem Gehalt an Vinylacetat zwischen 12 und 16% ist.

35. Verarbeitbare Lebensmittelunterbringung nach wenigstens einem der Ansprüche 32 und 34, worin das genannte Modifizierungsmittel (iii) von Holz stammender Flüssig-Rauch ist, dessen Farbe und Aroma auf die äußere Oberfläche des Lebensmittels während dessen Verarbeitung in der genannten Lebensmittelhülle übertragbar ist.

36. Verarbeitbare Lebensmittelunterbringung nach wenigstens einem der Ansprüche 32 und 34, worin das genannte Modifizierungsmittel (iii) ein Färbemittel ist, das auf die äußere Oberfläche des Lebensmittels während dessen Verarbeitung in der genannten Lebensmittelhülle übertragbar ist.

37. Verarbeitbare Lebensmittelunterbringung nach wenigstens einem der Ansprüche 32 bis 36, worin die genannte Mischung eine Schicht einer mehrschichtigen Folie ist, die wenigstens drei Schichten einschließlich einer Kern-Sperrschicht umfaßt: die Mischungsschicht, die an der inneren Oberfläche der genannten Kernschicht haftet, wobei die innere Oberfläche in direktem Kontakt mit der äußeren Oberfläche des genannten Lebensmittels steht, und eine dritte Polyolefinschicht, die an der äußeren Oberfläche der genannten Kernschicht haftet, wobei die genannte mehrschichtige Folie mit einer Dosis von wenigsten 2 MR bestrahlt sein kann.

38. Verfahren zur Herstellung eines übertragbaren Modifizierungsmittels als Folienprodukt, das die folgenden Schritte umfaßt:

a) Bereitstellung einer Harzmischung, die umfaßt: (i) ein thermoplastisches Polymer, ausgewählt aus Polyolefinen, Polyurethanen, Ionomeren, Polyamiden, Polyestern, Vinylidenchlorid-Copolymeren und hydrolysierten Ethylen-Vinylacetat-Copolymerenund (ii) Poly(ethylenoxid) mit einem durchschnittlichen Molekulargewicht von wenigstens 70.000,

b) Strangpressen der genannten Harzmischung zu einer Folie und

c) Absorbieren (iii) eines Modifizierungsmittels nach Anspruch 1 von der stranggepreßten Mischung.

39. Verfahren nach Anspruch 38, worin das genannte Poly(ethylenoxid) ein durchschnittliches Molekulargewicht von etwa 100.000 aufweist.

40. Verfahren nach wenigstens einem der Ansprüche 38 und 39, worin das genannte thermoplastische Polymer Polyolefin ist, vorzugsweise Ethylen-Vinylacetat (EVA) mit einem Gehalt an Vinylacetat von vorzugsweise zwischen 12 und 16 Gew.-%.

41. Verfahren nach Anspruch 40, worin das genannte Polyolefin eine Mischung eines ersten EVA mit einem Gehalt an Vinylacetat von weniger als 24 Gew.-% und einem zweiten EVA mit einem Gehalt an Vinylacetat von mehr als 8 Gew.-% umfaßt.

42. Verfahren nach Anspruch 40, worin das genannte Polyolefin eine Mischung aus EVA und Polyethylen, z. B. einem Polyethylen mit geringer oder mit sehr geringer Dichte ist.

43. Verfahren nach wenigstens einem der Ansprüche 38 und 39, worin das genannte thermoplastische Polymer Polyamid ist.

44. Verfahren nach wenigstens einem der Ansprüche 38 bis 43, worin die stranggepreßte Folie biaxial orientiert ist.

45. Verfahren nach wenigstens einem der Ansprüche 38 bis 44, worin ein Harz zum Schutz gegen Sauerstoff und ein thermoplastisches Harz bereit gestellt und separat zusammen mit der genannten Harzmischung stranggepreßt werden, um eine dreischichtige Folie zu bilden, die eine Sauerstoff-Sperrschicht, die Mischung als eine zweite Schicht, die an der einen Seite der genannten Sauerstoff-Sperrschicht haftet, und das thermoplastische Harz als eine dritte Schicht, die an der anderen, der Mischungsschicht gegenüberliegenden Seite der genannten Sauerstoff-Sperrschicht haftet, umfaßt.

46. Verfahren nach Anspruch 45, worin die stranggepreßte dreischichtige Folie biaxial orientiert ist.

47. Verfahren nach Anspruch 45, worin die stranggepreßte Folie mit einer Dosis von wenigstens 2 MR bestrahlt ist.

48. Verfahren nach wenigstens einem der Ansprüche 38 bis 47, worin das genannte Modifizierungsmittel ein Färbemittel, ein Aroma, ein farbgebendes Aroma, z. B. von Holz stammender Flüssig-Rauch, oder ein Biozid ist.

49. Verfahren zur Herstellung einer modifizierten Lebensmittelunterbringung, das die folgenden Schritte umfaßt:

a) Bereitstellung eines stranggepreßten Folienprodukts mit Wänden, die die Mischungen der Komponenten (i) bis (iii) nach Anspruch 1 umfassen, wobei das genannte Modifizierungsmittel (iii) in der genannten Mischung absorbiert ist;

b) Füllen des genannten Folienprodukts mit einem verarbeitbaren Lebensmittel, so daß die Möglichkeit eines Fluidtransfers zu der äußeren Oberfläche des Lebensmittels von der das Modizierungsmittel enthaltenen Folie besteht;

c) Verarbeitung der Lebensmittel-enthaltenden Unterbringung bei erhöhter Temperatur in Anwesenheit von umgebendem heißen Wasser, um das Lebensmittel zu kochen und gleichzeitig das genannte Modifizierungsmittel von der genannten Folienhülle zu der äußeren Oberfläche des mit Wasser behandelten Lebensmittels zu übertragen.

50. Verfahren nach Anspruch 49, worin das verarbeitbare Lebensmittel Feuchtigkeit enthält und sich dessen äußere Oberfläche in benachbartem Kontakt mit der das Modifizierungsmittel enthaltenden Folie befindet.

51. Verfahren nach wenigstens einem der Ansprüche 49 und 50, worin das genannte thermoplastische Polymer (i) Polyolefin, vorzugsweise Ethylen-Vinylacetat (EVA) mit einem Gehalt an Vinylacetat von vorzugsweise Zwischen 12 und 16% ist.

52. Verfahren nach wenigstens einem der Ansprüche 49 und 51, worin das genannte Polyolefin eine Mischung eines ersten EVA mit einem Gehalt an Vinylacetat von weniger als 24 Gew.-% und einem zweiten EVA mit einem Gehalt an Vinylacetat von weniger als des ersten EVA, jedoch mehr als 8 Gew.-% umfaßt.

53. Verfahren nach Anspruch 51, worin das genannte Polyolefin eine Mischung aus EVA und Polyethylen, z. B. einem Polyethylen mit geringer oder mit sehr geringer Dichte ist.

54. Verfahren nach wenigstens einem der Ansprüche 49 und 50, worin das genannte thermoplastische Polymer Polyamid ist.

55. Verfahren nach wenigstens einem der Ansprüche 49 bis 54, worin die stranggepreßte Folie biaxial orientiert ist.

56. Verfahren nach wenigstens einem der Ansprüche 49 bis 55, worin das genannte Modifizierungsmittel ein Färbemittel oder ein farbgebendes Aroma, z. B. von Holz stammender Flüssig-Rauch ist.

57. Verfahren nach Anspruch 56, worin die Farbe und der Geschmack von Rauch auf die äußere Oberfläche des Lebensmittels während der genannten Verarbeitung bei hoher Temperatur übertragen wird.

58. Verfahren nach wenigstens einem der Ansprüche 49 bis 57, worin die genannte Folienunterbringung eine mehrschichtige Folie einschließlich einer Kern-Sauerstoffsperrschicht umfaßt: die Mischungsschicht, die an der inneren Oberfläche der Sauerstoff-Sperrschicht haftet, um den direkten Kontakt mit der äußeren Oberfläche des Lebensmittels herzustellen, und eine andere Schicht, die aus thermoplastischem Material gebildet wurde und an der der äußeren Oberfläche der Sauerstoff-Sperrschicht haftet, wobei die genannten mehrschichtige Folientasche mit einer Dosis von wenigstens 2 MR bestrahlt ist.

59. Verfahren nach Anspruch 58, worin die genannte Komponente (i) der Mischung EVA mit einem Gehalt an Vinylacetat von zwischen 12 und 16 Gew.-% ist, die genannte Sauerstoff-Sperrschicht ein Vinylidenchlorid-Copolymer ist, die genannte thermoplastische Schicht ein Polyolefin ist, das genannte Modifizierungsmittel ein von Holz stammender Flüssig-Rauch ist und die Farbe und der Geschmack des Rauchs auf die äußere Oberfläche des Lebensmittels während der Verarbeitung bei hoher Temperatur übertragen wird.

Revendications

1. Article consistant en un film extrudé, comprenant un mélange (i) d'un polymère thermoplastique choisi entre des polyoléfines, des polyuréthannes, des ionomères, des polyamides, des polyesters, des copolymères de chlorure de vinylidène et des copolymères éthylène-acétate de vinyle hydrolysés, (ii) d'un poly(oxyde d'éthylène) ayant un poids moléculaire moyen d'au moins 70 000, et (iii) d'un modificateur choisi entre des colorants, des parfums, des agents aromatisants, des parfums colorants, des anti-oxydants pour inhiber le rancissement de denrées alimentaires, des agents antimycotiques, des biocides, des absorbants d'odeurs et des modificateurs d'énergie superficielle, ledit modificateur étant absorbé dans ledit mélange et étant transférable dudit film à une surface réceptrice en relation de transfert de fluide avec ledit film.

2. Article suivant la revendication 1, dans lequel le polymère thermoplastique est une polyoléfine, par exemple un polymère éthylène-acétate de vinyle (EVA) qui a de préférence une teneur en acétate de vinyle de 12 à 16 % en poids.

3. Article suivant la revendication 2, dans lequel la polyoléfine comprend un mélange d'un premier EVA ayant une teneur en acétate de vinyle inférieure à 24 % en poids et d'un second EVA ayant une teneur en acétate de vinyle inférieure à celle dudit premier EVA, mais supérieure à 8 % en poids.

4. Article suivant la revendication 3, dans lequel le mélange de polyoléfines comprend 40 à 60 % en poids du premier EVA et 40 à 60 % en poids du second EVA.

5. Article suivant au moins une des revendications 1 à 4, dans lequel la polyoléfine consiste en un mélange de EVA et de polyéthylène, par exemple de polyéthylène linéaire basse densité ou de polyéthylène très basse densité.

6. Article suivant la revendication 5, dans lequel le EVA a une teneur en acétate de vinyle de 8 % en poids à 24 % en poids, ledit EVA représente 70 % en poids à 90 % en poids du mélange, et le polyéthylène comprend 10 % en poids à 30 % en poids de polyéthylène très basse densité.

7. Article suivant la revendication 1, dans lequel le polymère thermoplastique est un polyamide.

8. Article suivant au moins une des revendications 1 à 7, dans lequel le poly(oxyde d'éthylène) a un poids moléculaire moyen d'environ 100 000.

9. Article suivant au moins une des revendications 1 à 8, dans lequel le poly(oxyde d'éthylène) représente au moins 10 % en poids du mélange, par exemple 15 % en poids à 40 % en poids dudit mélange.

10. Article suivant au moins une des revendications 1 à 9, dans lequel le modificateur est absorbé par le mélange après extrusion du film.

11. Article suivant au moins une des revendications 1 à 10, dans lequel le modificateur est un colorant, un parfum, un parfum-colorant ou un biocide.

12. Article suivant la revendication 11, dans lequel le parfum-colorant est une fumée liquide dérivée du bois.

13. Article suivant la revendication 12, dans lequel la fumée liquide a une teneur totale en acide d'au moins 10 %.

14. Article suivant au moins une des revendications 12 et 13, dans lequel la fumée liquide représente 10 % en poids à 40 % en poids dudit article.

15. Article suivant au moins une des revendications 1 à 14, dans lequel le mélange représente une couche d'un film multicouche.

16. Article suivant la revendication 15, dans lequel le film multicouche comprend au moins trois couches dont une couche centrale de barrière à l'oxygène, la couche formée du mélange sur une face de ladite couche de barrière, et une autre couche formée d'une matière thermoplastique sur l'autre face de ladite couche centrale de barrière à l'oxygène, le modificateur étant transférable de ladite couche formée par le mélange à la surface réceptrice en relation de transfert de fluide avec ladite couche formée par le mélange.

17. Film multicouche suivant la revendication 16, dans lequel la couche centrale de barrière à l'oxygène est formée d'un copolymère de chlorure de vinylidène.

18. Film multicouche suivant la revendication 16, dans lequel la couche centrale de barrière à l'oxygène est formée d'un polymère éthylène-alcool vinylique ou d'un mélange d'un polymère éthylène-alcool vinylique et d'un polyamide.

19. Film multicouche suivant au moins une des revendications 16 à 18, dans lequel le polymère thermoplastique présent dans la couche de mélange est une polyoléfine.

20. Film multicouche suivant au moins une des revendications 16 à 19, dans lequel le polymère thermoplastique présent dans la couche de mélange et le polymère thermoplastique présent dans l'autre couche sont formés d'une polyoléfine.

21. Film multicouche suivant au moins une des revendications 16 à 20, qui a subi une orientation biaxiale et qui est thermorétractable.

22. Film extrudé multicouche à orientation biaxiale et thermorétractable, comprenant une couche centrale de barrière constituée d'un copolymère de chlorure de vinylidène ; une deuxième couche de mélange adhérant à une face de la couche centrale et comprenant les constituants (i) à (iii) tels que définis dans la revendication 1, dans laquelle le constituant (i) est une polyoléfine, le modificateur (iii) étant transférable de la deuxième couche de mélange du film multicouche à une surface réceptrice contiguë en présence d'eau, et une troisième couche de polyoléfine adhérant à l'autre face de ladite couche centrale opposée à ladite première face.

23. Film multicouche suivant la revendication 22, dans lequel la polyoléfine des deuxième et troisième couches est un polymère éthylène-acétate de vinyle, et le modificateur est une fumée liquide dérivée du bois absorbée par le mélange après extrusion dudit film, la couleur et la saveur de la fumée liquide étant transférables à la surface contiguë.

24. Film multicouche suivant au moins une des revendications 16 à 23, qui est irradié à une dose d'au moins 2 MR.

25. Sac thermoplastique formé d'un film extrudé suivant la revendication 1, le modificateur (iii) étant transférable dudit film à une surface de réception de produit à l'intérieur dudit sac.

26. Sac thermoplastique formé d'un film multicouche extrudé comprenant une couche centrale de barrière ; une deuxième couche de mélange adhérant à la surface intérieure de la couche centrale et comprenant un premier constituant polyoléfinique et un second constituant du type poly(oxyde d'éthylène) ayant un

poids moléculaire moyen d'au moins 70 000 et une fumée liquide dérivée du bois absorbée dans ledit mélange, la couleur et la saveur de ladite fumée liquide étant transférables dudit film multicouche à une surface contiguë de réception de produit alimentaire à l'intérieur dudit sac en présence d'eau chauffée ; et une troisième couche de polyoléfine adhérant à la surface extérieure de la couche centrale.

27. Sac thermoplastique suivant au moins une des revendications 25 et 26, dans lequel le film multicouche est irradié à une dose d'au moins 2 MR.

28. Enveloppe thermoplastique formée d'un film extrudé suivant la revendication 1, le modificateur (iii) étant transférable dudit film à une surface de réception de produit à l'intérieur de ladite enveloppe.

29. Enveloppe thermoplastique formée d'un film multicouche extrudé comprenant une couche centrale de barrière ; une deuxième couche de mélange adhérant à la surface intérieure de la couche centrale et comprenant un premier constituant polyoléfinique et un second constituant du type poly(oxyde d'éthylène) ayant un poids moléculaire moyen d'au moins 70 000, comprenant une fumée liquide dérivée du bois absorbée dans ledit mélange, la couleur et la saveur de ladite fumée liquide étant transférables dudit film multicouche à une surface contiguë de réception de produit alimentaire à l'intérieur de ladite enveloppe en présence d'eau chauffée ; et d'une troisième couche de polyoléfine adhérant à la surface extérieure de ladite couche centrale.

30. Enveloppe suivant au moins une des revendications 28 et 29, qui est plissée.

31. Enveloppe thermoplastique suivant au moins une des revendications 29 et 30, dans laquelle le film multicouche est irradié à une dose d'au moins 2 MR.

32. Emballage pour produit alimentaire à traiter, comprenant une enceinte constituée d'un film thermoplastique extrudé, remplie avec un produit alimentaire à traiter, dont la surface extérieure est en relation de transfert de fluide avec la surface intérieure de l'enceinte constituée d'un film, ladite enceinte constituée d'un film comprenant le mélange des constituants (i) à (iii) répondant à la définition suivant la revendication 1, et le modificateur (iii) étant transférable de ladite enceinte constituée d'un film à la surface extérieure du produit alimentaire lorsque ce produit est traité dans ladite enceinte constituée d'un film.

33. Emballage pour produit alimentaire à traiter, suivant la revendication 32, dans lequel ledit produit alimentaire à traiter contient de l'humidité et sa surface extérieure est en contact contigu avec la surface intérieure de l'enceinte constituée d'un film.

34. Emballage pour produit alimentaire à traiter, suivant au moins une des revendications 32 et 33, dans lequel le polymère thermoplastique (i) est un polymère éthylène-acétate de vinyle ayant une teneur en acétate de vinyle comprise dans l'intervalle de 12 à 16 % en poids.

35. Emballage pour produit alimentaire à traiter, suivant au moins une des revendications 32 et 34, dans lequel le modificateur (iii) est une fumée liquide dérivée du bois, dont la couleur et la saveur sont transférables à la surface extérieure du produit alimentaire lorsque ce produit est traité dans ladite enceinte pour produit alimentaire.

36. Emballage pour produit alimentaire à traiter, suivant au moins une des revendications 32 à 34, dans lequel le modificateur (iii) est un colorant dont la couleur est transférable à la surface extérieure du produit alimentaire lorsque ce produit est traité dans ladite enceinte pour produit alimentaire.

37. Emballage pour produit alimentaire à traiter, suivant au moins une des revendications 32 à 36, dans lequel le mélange constitue une couche d'un film multicouche formée d'au moins trois couches comprenant une couche centrale de barrière, la couche de mélange adhérant à la surface intérieure de ladite couche centrale avec sa surface intérieure en contact direct avec la surface extérieure du produit alimentaire, et une troisième couche de polyoléfine adhérant à la surface extérieure de ladite couche centrale, ledit film multicouche pouvant être irradié à une dose d'au moins 2 MR.

38. Procédé de production d'un article consistant en un film avec un modificateur transférable, comprenant les étapes consistant :

a) à prendre un mélange de résines comprenant (i) un polymère thermoplastique choisi entre des polyoléfines, des polyuréthannes, des ionomères, des polyamides, des polyesters, des copolymères de chlorure de vinylidène et des copolymères éthylène-acétate de vinyle hydrolysés, et (ii) un poly-(oxyde d'éthylène) ayant un poids moléculaire moyen d'au moins 70 000,

b) à extruder ledit mélange de résines en un film, et

c) à provoquer l'absorption d'un modificateur (iii) répondant à la définition suivant la revendication 1 dans le mélange extrudé.

39. Procédé suivant la revendication 38, dans lequel le poly(oxyde d'éthylène) a un poids moléculaire moyen d'environ 100 000.

40. Procédé suivant au moins une des revendications 38 et 39, dans lequel le polymère thermoplastique est une polyoléfine, de préférence un polymère éthylène-acétate de vinyle (EVA) ayant une teneur en acétate de vinyle comprise de préférence dans l'intervalle de 12 à 16 % en poids.

41. Procédé suivant la revendication 40, dans lequel la polyoléfine comprend un mélange d'un premier EVA ayant une teneur en acétate de vinyle inférieure à 24 % en poids et d'un second EVA ayant une teneur en acétate de vinyle supérieure à 8 % en poids.

42. Procédé suivant la revendication 40, dans lequel la polyoléfine est un mélange de EVA et de polyéthylène, par exemple de polyéthylène linéaire basse densité ou très basse densité.

43. Procédé suivant au moins une des revendications 38 et 39, dans lequel le polymère thermoplastique est un polyamide.

44. Procédé suivant au moins une des revendications 38 à 43, dans lequel le fim extrudé a subi une orientation biaxiale.

45. Procédé suivant au moins une des revendications 38 à 44, dans lequel une résine servant de barrière à l'oxygène et une résine thermoplastique sont utilisées et extrudées séparément avec ledit mélange de résines pour former un film en trois couches comprenant une couche de barrière à l'oxygène, le mélange servant de deuxième couche adhérant à ladite couche de barrière à l'oxygène sur une de ses faces, et la résine thermoplastique servant de troisième couche adhérant à ladite couche de barrière à l'oxygène sur son autre face à l'opposé de la couche de mélange.

46. Procédé suivant la revendication 45, dans lequel le film extrudé en trois couches a subi une orientation biaxiale.

47. Procédé suivant la revendication 45, dans lequel le film extrudé est irradié à une dose d'au moins 2 MR.

48. Procédé suivant au moins une des revendications 38 à 47, dans lequel le modificateur est un colorant, un parfum, un parfum-colorant, par exemple une fumée liquide dérivée du bois, ou un biocide.

49. Procédé de production d'un emballage modifié pour produit alimentaire, comprenant les étapes consistant :

a) à prendre un article consistant en un film extrudé ayant des parois comprenant le mélange des constituants (i) à (iii) répondant à la définition suivant la revendication 1, le modificateur (iii) étant absorbé dans ledit mélange ;

b) à remplir l'article sous forme de film avec un aliment à traiter, de telle sorte que la surface extérieure de l'aliment soit en relation de transfert de fluide avec le film contenant le modificateur ;

c) à traiter l'emballage contenant le produit alimentaire à température élevée en présence d'eau chauffée environnante pour cuire ledit produit alimentaire et transférer simultanément ledit modificateur dudit emballage sous forme de film à la surface extérieure de l'aliment cuisiné en présence d'eau.

50. Procédé suivant la revendication 49, dans lequel le produit alimentaire à traiter contient de l'humidité et sa surface extérieure est en contact contigu avec le film contenant le modificateur.

51. Procédé suivant au moins une des revendications 49 et 50, dans lequel le polymère thermoplastique (i) est une polyoléfine, de préférence un polymère éthylène-acétate de vinyle (EVA) ayant une teneur en acétate de vinyle comprise de préférence dans l'intervalle de 12 à 16 % en poids.

52. Procédé suivant au moins une des revendications 49 et 51, dans lequel la polyoléfine comprend un mélange d'un premier EVA ayant une teneur en acétate de vinyle inférieure à 24 % en poids et d'un second EVA ayant une teneur en acétate de vinyle inférieure à celle dudit premier EVA, mais supérieure à 8 % en poids.

53. Procédé suivant la revendication 51, dans lequel la polyoléfine est un mélange de EVA et de polyéthylène, par exemple de polyéthylène linéaire basse densité ou de polyéthylène très basse densité.

54. Procédé suivant au moins une des revendications 49 et 50, dans lequel le polymère thermoplastique est un polyamide.

55. Procédé suivant au moins une des revendications 49 à 54, dans lequel le film extrudé a subi une orientation biaxiale.

56. Procédé suivant au moins une des revendications 49 à 55, dans lequel le modificateur est un colorant ou un parfum-colorant, par exemple une fumée liquide dérivée du bois.

57. Procédé suivant la revendication 56, dans lequel la couleur et la saveur de la fumée sont transférées à la surface extérieure du produit alimentaire lorsque ce produit alimentaire est traité à haute température.

58. Procédé suivant au moins une des revendications 49 à 57, dans lequel l'emballage sous forme de film consiste en un film multicouche comprenant une couche centrale de barrière à l'oxygène, la couche de mélange adhérant à la couche de barrière à l'oxygène sur la surface inférieure de cette couche pour le contact direct avec la surface extérieure du produit alimentatire, et une autre couche formée d'une matière thermoplastique adhérant à la couche de barrière à l'oxygène sur la surface extérieure de cette couche, ledit sac sous forme d'un film multicouche étant irradié à une dose d'au moins 2 MR.

59. Procédé suivant la revendication 58, dans lequel le constituant (i) du mélange est un polymère EVA ayant une teneur en acétate de vinyle de 12 à 16 % en poids, la couche de barrière à l'oxygèn est constituée d'un copolymère de chlorure de vinylidène, la couche thermoplastique est constituée d'une polyoléfine, le modificateur est une fumée liquide dérivée du bois, et la couleur et la saveur de la fumée sont transférées à la surface extérieure du produit alimentaire lorsque ce produit est traité à haute température.